Raw material resources, like minerals and metals, underpin the functioning of the European and global economy and inescapably govern the quality of life in each society. In the recent years the term "critical" raw materials has been applied to further signify raw materials with both economic importance and predicted supply risk. Among them the Rare Earth Elements (REE), 17 chemically similar metallic elements, including the 15 lanthanides, scandium and yttrium.

The REEs are used in a wide range of applications, including metallurgy (metal refining and metal alloying), catalysts in the automotive and the petro-chemical industry, colouring of glass/ceramics, phosphors (LEDs, compact fluorescent lamps, flat panel displays), lasers, rechargeable solid state batteries (Ni-MH), fiber optics and others. Additionally, REE are vital components in emerging technologies such as solid state fuel cells, superconductors, magnetic cooling, hydrogen storage and high performance permanent magnets. With constantly increasing applications ranging from micro-electronics to wind generators and with very few rare earth mines in operation around the world, the rare earth elements supply and demand is in the global spotlight.

As result, in the last four years there has been both intense political and research activity in Europe for exploring potential European REE resources and developing novel processing and recycling technologies. Under the framework of the EURARE: Development of a sustainable exploitation scheme for Europe’s rare earth ore deposits project, this scientific conference on European Rare Earth Resources is now being organized with the hope that it may serve as the ground for exchanging ideas, networking different groups and furthering academic and applied knowledge on European Rare Earth Resources.
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EURARE: Development of a sustainable exploitation scheme for Europe’s rare earth ore deposits

The main goal of the EURARE project is to set the basis for the development of a European REE industry that will safeguard the uninterrupted supply of REE raw materials and products to crucial for the EU economy industrial sectors, such as automotive, electronics, machinery and chemicals, in a sustainable, economically viable and environmentally friendly way. 23 partners from 10 different European countries comprise the multi-actor EURARE consortium.

The EURARE project has received funding from the European Community's Seventh Framework Programme ([FP7/2007-2013]) under grant agreement n°309373. Project website: www.eurare.eu

RARE³: Research Platform for the Advanced Recycling and Reuse of Rare Earths

This KU Leuven funded project targets breakthrough recycling processes based on non-aqueous technology for the two main applications of rare earths: permanent magnets and lamp phosphors. This work is part of a more general objective to create fully integrated, closed-loop recycling flow sheets. The knowledge platform is steered by an Industrial User Committee, which includes more than 30 US, EU and Flemish players in the field of REEs. Moreover, these companies are situated at all different levels of the REE value chain, from ore extraction, separation, production of consumer goods to recycling.

The RARE³ project project is funded from the KU Leuven. Project website: http://kuleuven.rare3.eu
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Session I: Rare Earth Resources
THE RARE EARTH CRISIS AND THE CRITICAL MATERIALS INSTITUTE’S (CMI’S) ANSWER

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Abstract

The Critical Materials Institute (CMI) of the Ames Laboratory is a U.S. Department of Energy (DOE) Innovation Hub dealing with energy critical materials. At the present time CMI is concerned with five rare earth materials (yttrium, neodymium, europium, terbium and dysprosium), and lithium and tellurium. The Institute has four focus areas - (1) diversifying supply, (2) developing substitutes, (3) improving reuse and recycling, and (4) crosscutting research. There are four national DOE laboratories involved (lead by the Ames Laboratory, together with Idaho National Laboratory, Lawrence Livermore National Laboratory and Oak Ridge National Laboratory), six industrial organizations and seven universities.

Extended Abstract

In response to a Department of Energy Funding Opportunity Announcement (FOA) on critical materials a consortium, called the Critical Materials Institute (CMI), lead by the Ames Laboratory was informed on January 8, 2013, that they were selected as the latest DOE Energy Innovation Hub. The actual start date of CMI was June 1, 2013.

The CMI is composed of four focus areas: (1) diversify the global supply chain, (2) develop substitute materials, (3) enhance recycling, reuse and efficient use of materials, and (4) crosscutting research. The CMI is led by Alex King (Ames Laboratory), Director; Rod Eggert (Colorado School of Mines), Deputy Director; and Karl Gschneidner (Ames Laboratory), Chief Scientist. The CMI consortium is composed of four national DOE laboratories, six industrial organizations, and seven academic institutions. The four national laboratories are: the Ames Laboratory, Oak Ridge National Laboratory, Idaho National Laboratory and Lawrence Livermore National Laboratory. The six companies are: Advanced Recovery, Inc., Cytec, General Electric
Co., Molycorp, OLI Systems, Inc., and Simbol Materials. The academic institutions are: Rutgers University, University of California-Davis, Colorado School of Mines, Brown University, Iowa State University, Florida Institute of Phosphate Research, and Purdue University. CMI’s mission is to eliminate materials criticality as an impediment to the commercialization of clean energy technologies for today and tomorrow.

The CMI addresses seven critical or near-critical chemical elements: yttrium, neodymium, europium, terbium, dysprosium, lithium, and tellurium. Of these seven elements only the five rare earth metals are on the European Critical Raw Materials list. Initially 35 projects were selected for study by applying several criteria: potential for impact at a key point in a material’s lifecycle in a realistic timeframe; integration of strengths and capabilities across the Hub; a clear path to deployment, i.e. commercialization plan in place; an annual evaluation to address continued adherence to the timeline and the above criteria. As things change projects are expected to be terminated and new ones started.

Focus area 1 (diversifying supply) has three thrusts: new sources, transformational processes, and new uses for co-products. Within the three thrusts there are eight projects.

Focus area 2 (developing substitutes) has three thrusts: magnets, lighting, and materials development framework. In this focus area there are nine projects.

Focus area 3 (improving reuse and recycling) has only two thrusts, but nine projects. The two thrusts are: source separation and concentration, and transformative extraction and materials production.

Focus area 4 (crosscutting research) consists of three thrusts and nine projects. The three thrusts are: enabling science; environmental sustainability; and supply chain, economic analysis and policy.

Within the 35 CMI Projects there are 125 tasks being carried out by about 200 scientists, engineers, and technicians at the various organizations in the USA. This amounts to about 80 full-time equivalent technical and 20 full-time equivalent support personnel. As a result of recent both internal and external reviews several CMI projects were combined to improve the interactions between the staff working on related topic reducing the number of Projects to 30. Furthermore, tellurium was dropped as one of the seven critical elements because the company who was going to manufacture CdTe photovoltaic solar cells for energy conversion decided to use other photovoltaic materials. Also, the funding for several projects were reduced and may be zeroed out in the next 6 to 12 months depending upon meeting milestones. At least...
two new projects are expected to start in the second year, but they have not been announced.

During the first year of operation the staff of the Institute disclosed 10 inventions for possible patent protection.

The Critical Materials Institute offers a variety of educational opportunities through several partners. In particular Colorado School of Mines offers several short courses such as Recycling Metals from Industrial Waste, and Mineral Processing. While Iowa State University offers a broad based course on the rare earths, which is available for distance learning.

The Critical Materials Institute has a membership program in which organizations can be involved as a Team Member, an Affiliate Member or an Associate Member. Team members have either research subcontracts from CMI or provide cost sharing funds. Affiliates (full or observing), through paid membership in the CMI, are informed about CMI research outcomes, may submit proposals for funding graduate student projects, and provide input to CMI. Associates are entities who want to access the unique capabilities and expertise of the CMI on a one-time basis. Associates, Team and Affiliate members may provide funding for a specific project via a Cooperative Research and Development Agreement (CRADA) or a Work for Others (WFO) agreement; all research agreements are done on a best effort basis and with full cost recovery.
THE ROLE OF EARTH SCIENCE FOR THE SUPPLY OF RARE EARTH ELEMENTS

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Abstract

Earth Science can play an important role in various stages of rare earth elements production, including target defining, geochemical prospecting, evaluation of mineral resource and reserve, beneficiation, etc. This is because of the limited experience in the exploration and exploitation of REE by exploration and mining companies outside China, compared to the other metal commodities. In particular, some of the heavy rare earth elements demanded by the industry are new targets for the companies. However, ongoing vast researches on the occurrence, behaviour, concentration and extraction of REE will be able to ease the criticality of REE in near future.

Introduction

The Behaviour of rare earth elements (REE) in melts and fluids have been widely applied in earth science as tracer of magmas genesis and evolution, index of oxidation state of magmas and fluids, geochronology (Sm-Nd radiometric dating), etc. Despite the wide recognition of the behaviour of REE in magmas and fluids, it has not been well understood how REE are transported, fractionated and concentrated to form economic-grade rare earth deposits. For example, why only a few carbonatites such as Mountain Pass and Bayan Obo possess ore-grade rare earth concentration¹, which ligand (fluorine, chlorine, etc.) is most important for the transportation of REE in magmas and fluids², are still debated. Now vast researches on the occurrence, behaviour, concentration of REE are ongoing, and wide spectrum of knowledge is accumulating.

Recent development of rare earth products used in high-technology and/or new materials (NdFeB magnets, semiconductor, ceramic knives, fuel cell, etc.) has
demanded not only the light rare earth elements (LREE; La-Eu) but also some of the heavy rare earth elements (HREE; Gd-Lu + Y) such as Dy, Tb and Y. Those HREE have not been well explored in the history, except for xenotime in placer sands along continental coasts and ion-adsorption type deposits in southern China. Thus, new exploration and exploitation projects of HREE meet a lot of challenges. Earth science can contribute to such projects to overcome difficulties in providing exploration strategy, knowledge of mineralogy and mineral chemistry, as well as ore mineral beneficiation. This paper presents some examples that scientific researches contributed to the REE (especially HREE) exploration projects.

**Project targeting**

**World resource database**

Until the progress of many REE exploration projects in recent years, there was no dataset that show the resource potential of the individual REE such as Nd, Pr, Dy and Tb that are used for the production of NdFeB magnets. A preliminary attempt was made in 2006 to evaluate the resource of such specific elements to reveal potential regions on the basis of the available datasets that compiled whole rare earth resources of individual deposits in the world\(^3\). The result shows that Brazil has the greatest potential of Nd and Pr, and three regions, Canada, southern Africa and Saudi Arabia, have good potential of Dy and Tb (Figure 1). Such new data were used for targeting exploration regions for HREE.

**Figure 1:** Calculated Nd, Pr, Dy and Tb resources based on the data available before 2006. The amounts of Nd and Pr, and Dy and Tb are combined together, respectively.
Favourable lithology and environment

The present production of HREE is dominated from ion-adsorption deposits in southern China. This-type deposits are formed in weathering profiles of granite and felsic volcanic rocks. Rare earth elements absorbed on clay minerals formed by weathering are easily leached with diluted ammonium sulphate solutions. For this reason, the weathering profiles containing more than 500 ppm ion-exchangeable REE with commercially significant sizes (area and thickness) are considered as ores. Recent studies show that HREE are concentrated in fractionated ilmenite-series granites, and rare earth elements are present as secondary fluorocarbonates in addition to refractory apatite and allanite in the host granites of the ion-adsorption deposit areas. Thus, favourable conditions to form HREE-enriched ion-adsorption deposits are 1) tectonically stable and tropical to semi-tropical climate regions to preserve thick weathering profiles, and 2) regions of fractionated ilmenite-series granitoids, which underwent deuteric alteration to form fluorocarbonates to supply ion-exchangeable REE to the profiles. The exploration strategy based on these results leads to the discovery of ion-adsorption type mineralization in Southeast Asia such as Vietnam and Thailand.

It has been well known that HREE are typically concentrated in peralkaline rock complexes, in particular, in the most fractionated parts of the complexes with other HFSE such as Zr and Nb. Accumulated mineralogical and geochemical knowledge by scientific researches immediately leads to the exploration projects in the regions (northeast Canada, Greenland, and southern Africa) where peralkaline rock complexes are common. These projects are supported by continuous geochemical and mineralogical studies at Strange Lake, Thor Lake, etc., which provide indispensable information for mineral concentration and REE extraction.

Geochemical prospecting

Recent spread of portable XRF analyser in geochemical prospecting has enabled us to detect low grade REE mineralization. Comparison of the chemical data obtained by portable XRF with the results by ICPMS in the laboratory shows that La and Ce is detectable as low as 150 ppm and Y as low as 30 ppm for the ion-adsorption clay samples (Figure 2). These results show that portable XRF analyser is effective in the survey of ion-adsorption and other type REE deposits, in particular, HREE exploration, because Y detection limit is lower than La and Ce. This method was applied to delineate Y anomalies in a fluorspar prospect in South Africa (Figure 3).
Figure 2: Comparison of analytical results by portable XRF and ICPMS for the samples of ion-adsorption clay in Conception, Chile. Vertical and horizontal axes are the results by XRF and ICPMS, respectively.

Figure 3: Y concentration (ppm) in termite mounds in the Blockspruit prospect in South Africa, measured by portable XRF analyser.

Mineralogy and mineral chemistry

A number of rare earth minerals are present in alkaline rock complexes and pegmatites, and detailed mineralogical works are indispensable for the recovery of these minerals. Some of the minerals contain minor amounts of REE and if these minerals contain important elements (Dy, Tb), they become a target for exploration and exploitation. It has been known that zirconium silicates are occasionally concentrated in HREE, although, these minerals have not been regarded as a resource source until recently, due to scarcity of geochemical data and lack of the established beneficiation methods. Recent advance in trace element quantitative analysis by LA-ICPMS has made it easier to determine rare earth concentration in such minerals.

The Jabal Tawlah deposit in Saudi Arabia is reported to be HREE-concentrated microgranite with Nb and Zr in the Proterozoic sedimentary rocks. The granite forms a small sill-like body with 330m extension and a maximum thickness of 50m, and 6.4Mt of ore is estimated. The microgranite is heavily fractionated and is composed of quartz, albite and microcline with accessory zircon, Nb oxides and REE minerals. Total
REE content including Y is about 1.2wt% as oxides. Major ore minerals are columbite, fergusonite, Ca-Y-F minerals, and xenotime. A mineralogical study shows that Ca-Y-F minerals are composed of waimirite-(Y) (YF₃) and a Ca-Y-F undetermined phase (Figure 4). Waimirite¹⁹ is a mineral approved by IMA in December 2013, and nearly half of REE in the deposit is present in these new and undetermined phases, sharing the other half with xenotime. The deposit is regarded to be the highest Dy grade deposit in the world.

Figure 4: SEM image of Ca-Y-F phase and waimirite-(Y) (a) and chemical compositions of these minerals determined by EPMA. The compositions of tveitite-(Y) from Norway and Russia are also shown.

One of the target minerals for HREE extraction is eudialyte that contains a few to 10 wt% of REE. Because eudialyte is relatively enriched in HREE and occur abundantly in peralkaline complexes, several projects aim to produce REE from eudialyte. However, the REE content in eudialyte is variable even in the same unit of an intrusion and precise chemical analysis is necessary. An example is the Ilímaussaq peralkaline complex in Greenland, discovery place of eudialyte, which is divided into lower kakortokite and upper lujavrite. The REE compositions of eudialyte determined by LA-ICPMS show that eudialytes in the kakortokite and lujavrite contain 2.2-2.3wt% and 4.1-4.9wt% REE, respectively²⁰.

A whole rock analytical method using LA-ICPMS newly developed is to use a glass bead ablation method similar to XRF techniques¹⁷. This method has several advantages: 1) higher sensitivity than that achieved by the XRF method, 2) obviation of erroneous measurements due to incomplete dissolution of heavy minerals, and 3) simple and rapid sample preparation procedures for the analysis of both major and trace elements. The precisions of this method are better than 10% for Y, La, Pr and 20% for the other REE, and the method can provide REE compositional data of rocks faster than conventional ICPMS analysis.
Extraction

The extraction techniques of REE from conventional minerals (bastnäsite, monazite, xenotime) and ion-adsorption clay were well established\(^{21,22}\). However, to establish economically feasible REE extraction methods for other unconventional minerals are challenging.

Apatite

It has been known that apatite contain minor amounts of REE\(^ {23}\), and REE by-production has been explored in the process of phosphoric acid production. The methods using hydrochloric or nitric acid can extract more than 80% of REE, but when sulphuric acid is used, recovery of REE is low because majority of REE is incorporated into gypsum residue\(^ {24}\). Various attempts are being conducted for the extraction of REE from apatite, including a hydrochloric acid method\(^ {25}\).

Zircon

Zircon is a refractory mineral and generally contains less than 1wt% of REE, however, many varieties of zircon containing a large amount of REE, Th, U, Nb and Ta have been reported from peralkaline rocks and granites\(^ {13}\). A REE extraction experiment indicates that more than 90% of REE can be leached out from REE-bearing metamict zircon with 1M-HCL solution at temperature of 150°C\(^ {26}\).

Conclusion

Earth Science can play an important role for the supply of REE, by providing exploration strategy, target determination, geochemical prospecting, evaluation of resource and reserve, and beneficiation. This is because the exploration and mining experience is still immature for the mining sectors outside China. However, abrupt increase of REE demand, in particular, some specific elements such as Dy and Tb, urged industrialised countries to secure raw REE materials. Vast scientific researches are ongoing to clarify the occurrence, behaviour, concentration of REE in rocks, minerals, and solutions, which will be able to ease the criticality of REE in near future.

References

EXTRACTION AND RECOVERY OF RARE EARTH METALS: CHALLENGES IN PROCESSING

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Abstract

Rare earths metals, including yttrium and scandium, are being increasingly used in clean energy technologies, colored phosphors, lasers and high intensity magnets. The commitment to clean energy technologies by governments and the projected growth in power and transportation sectors across the globe ensure that the demand for rare earth metals and compounds would continue to escalate. This demand implies that, to ensure unhindered technological innovation, it is essential to possess secure supply chains for rare earth elements. In order to ensure secure rare earth supply and attenuate supply-demand imbalance post 2014, it is of utmost importance to look at opportunities to process intelligently, recycle and reuse Rare Earth Elements from secondary sources, such as post-consumer and manufacturing process wastes.

Introduction

Increasingly, the U.S. government, academia, domestic industry, and the public acknowledge the imperative that we need to conserve energy and natural resources while exercising judicious stewardship of the environment. The issue of sustainability is and should be paramount in how we design, manufacture, use, and retire the many products we consume throughout the world. Inorganic materials are not renewable; the need exists for the development of technologies to address materials recovery and recycling. Research supporting materials recovery and recyclability is inherently multidisciplinary and must respond to the needs of a multiplicity of commercial stakeholders from throughout the materials supply chain.

Despite growing efforts to recycle metals, we fail to recover half of the domestic post-consumer metal scrap reclaimable from retired products, and we continue to rely on primary metals production to fulfil two thirds of our manufacturing needs. Use of primary metals, in lieu of scrap, increases global energy consumption as well as the production of greenhouse gases. In order to augment recycling rates the materials community needs to upgrade recovery and recycling processing technologies to maximize the capture of post-consumer scrap and minimize the quantity of manufacturing scrap.
Rare earth elements are a group of 17 elements, which include 15 Lanthanides, Scandium and Yttrium. In spite of what the name suggests these elements are not “rare”. However, in recent years rare earth elements have become strategically critical for developed and developing economies around the world which is primarily due to the shortage of discovered minable resources\(^1\). Before 1948, the placer deposits of Brazil and India were the chief sources of rare earth metals for the rest of the world. With increasing demand newer supply sources were needed and for a while the monazite deposits in South Africa played an important role before the production was dominated by Bastnasite reserves in Mountain Pass and China\(^2\).

According to a forecast done by IMCOA, the world rare earth demand is projected to rise to 200,000 tons by 2014 and the Chinese production is expected to be around 160,000 tons\(^3\). In addition, the demand of rare earths in China itself has increased by 380% between 2000 and 2009, which is believed to be the primary reason behind the export cuts on rare earth\(^4\). These developments have made rare earth elements a strategically important material as evident by the Rare Earths and Critical Material Revitalization Act of 2010 approved on September 29, 2010 which aims to establish an R&D program within the DOE to assure long term supply of rare earth materials\(^5\). The US Department of Energy published an analysis of the criticality of selected rare metals, the most critical elements were identified to be Dysprosium, Neodymium, Terbium, Yttrium and Europium - what are also known as the heavy rare earth elements\(^6\). Based on the demand and supply position of common rare-earths, the prices of common metals like Ce, Nd, Sm, La and Y, went up by 150% to 700% in a short period of six months between January and August 2010.

**Preparation of Rare Earth Oxides**

Rare earth oxides can be produced by five commonly used methods: selective oxidation, selective reduction, fractional crystallization, ion exchange and solvent extraction.

**Selective Oxidation**: The rare earth metals that can be separated by selective oxidation are cerium, praseodymium and terbium. Selective oxidation is effective for these three rare earth metals because they can be oxidized from trivalent state to a tetravalent state, which allows for separation. The most commonly used oxidizing agents used for these reactions are persulfates, permanganate and hypochlorite. Air or oxygen is also used as an oxidizing agent\(^1\). In the selective oxidation of praseodymium and terbium, Pr (IV) and Tb (IV) will precipitate out of solution as rare earth oxides and settle because the tetravalent states for praseodymium and terbium are not stable in an aqueous solution. Whereas, in the selective oxidation of cerium,
the tetravalent cerium must be separated from the rare earth mixture by selective
dissolution of trivalent elements in a dilute acid or complete dissolution of the species
in a concentrated acid followed by precipitation. The tetravalent cerium can be
precipitated from the acidic solution through pH control.2

Selective Reduction: The rare earth metals that can be separated by selective
reduction are samarium, europium and ytterbium. Selective reduction is effective for
these three rare earth metals because they can be reduced to a divalent state. McCoy
developed the commercially used method for selective reduction of Eu. In this
method, Eu (III) is reduced to Eu (II) by zinc in a chlorine solution. The divalent Eu is
precipitated from the solution as a sulfate and is then dissolved in HCl, which causes
the formation of an oxide.3 This method does not work for samarium or ytterbium
because zinc does not reduce these metals. Marsh developed the commercially used
method for the selective reduction of ytterbium and samarium. In this method, rare
earth mixtures are placed in an acetate solution. Samarium and europium can then
be separated by reductive extraction into dilute sodium amalgam4.

Fractional Crystallization: Fractional crystallization is a process of separating the
components of a solution on the basis of their different solubilities. In this method,
the solution is evaporated until the least soluble component in solution crystallizes
out. In the fractional crystallization of rare earths, rare earth solutions are mixed with
a salt and then heated. The solutions are then allowed to gradually cool so that rare
earth oxide crystallizes out of solution. This method is usually most suitable for lanthanides at the lower end of the series.4 Ammonium nitrate salts are commonly
used for the separation of praseodymium and neodymium from solutions. Double
magnesium nitrates are commonly used for the separation of samarium, europium,
gadolinium and the ceric group. Bromates and ethyl sulfates are used in the
separation of the yttric group.5

Ion Exchange: Ion exchange reactions are a two-step process that involves the
interchange of ions between an aqueous solution and an insoluble resin. The first step
is absorption, which removes the metal ions from the solution and the second step is
elution, which is the recovery of metal compounds from the resin bed. This method
suitable for rare earth separation on a small scale because it is a batch process. A
commercially used ion exchange method involves the recovery of rare earth
compounds through the use of amberlite type resins and elution with completing
agents such as citric acid. EDTA and HEDTA are two other commonly used completing
agents because most all rare earth combinations can be successfully separated
through the use of these two agents.5

Solvent Extraction: Solvent extraction is the most economical method for separating
rare earth metals today. In solvent extraction, an aqueous solution is mixed with an
immiscible organic solvent. The metal is then transferred to the organic phase and
there is a phase separation due to the different densities. In the solvent extraction of rare earth metals, the aqueous solution contains the desired metals to be separated, which are subsequently transferred to the organic phase. The organic extractants used in this method can be classified as neutral, acidic, basic or a chelating agent. Neutral organic extractants generally yield low separation factors, which make them suitable for the recovery of mixed rare earth oxides. TBP (tributyl phosphate) is the most commonly used neutral extractant. Basic organic extractants are used to recover anionic lanthanides from aqueous solutions. Acidic extractants are very powerful and can be used to separate most rare earth metals. DEPHA is the most commonly used acidic extractant because it can be used to recover rare earth compounds from many different types of solutions\(^6\).

**Methods for producing rare earth metals**

The three primary methods practiced for producing pure rare earth metals from compounds. These three methods are (1) reduction of anhydrous chlorides and fluorides (2) direct reduction of rare earth oxides, and (3) fused salt electrolysis of rare earth chlorides or oxide fluoride mixtures\(^6\).

**Direct Reduction of Rare Earth Oxides:** Direct reduction of rare earth oxides process does not require the pre-transformation of the rare earth oxides into halides. The earliest attempts to directly reduce rare earth oxides to metals were made between 1890 and 1912 by Winckler, Matignon, and Hirsch. They used magnesium or calcium as a reducing agent for the rare earth oxides. Although, this method proved to be ineffective because the resulting mixture consisted of magnesium oxide or calcium oxide and a metal, which could not be separated. Several years later, Mahn revisited the magnesium reduction route. His method was to dip blocks of rare earth oxides in magnesium that was heated to 1050 °C. Although the magnesium metal attacked the metal oxide block, the only products obtained were very dilute solutions of rare earth metals in magnesium\(^2\).

In 1953, a major breakthrough was made by Daane for the reduction of volatile rare earth metals. In this process, rare earth oxides are mixed with lanthanum chips in a tantalum crucible fitted with a tantalum condenser. The mixture is heated to high temperature under vacuum so that the metal produced by the lanthanum reduction sublimes as crystalline condensates on the crucible wall. The metal was then collected from the crucible wall. The metal contained residual La, O, and H, but these impurities were removed by subliming the metal once more\(^7\). Onstatt also used this reduction - distillation method, but he used calcium instead of lanthanum as the reducing agent. This method turned out to be less effective than the lanthanum method because the metal had to be distilled three to four times in order to remove the majority impurities and the metal was only around 40%. Achard experimented using carbon as the reducing agent for the reduction – distillation process, but the distilled product from
this process contained high amounts of oxygen. Achard found that a second distillation at a higher pressure resulted in purer rare earth metals\(^2\).

In 1988, General Motors developed a molten salt process for the direct reduction of rare earth metals. To perform this process, a rare earth oxide is placed inside a reaction vessel with calcium chloride and sodium chloride. The sodium chloride is used to reduce the calcium chloride to calcium metal. The calcium metal then is used to reduce the rare earth oxide to a rare earth metal. The reaction vessel is then heated to a temperature above the melting point of the constituents but below the vaporization temperature of the sodium metal. The molten constituents must be rapidly stirred in order to keep them in contact with one another. As the reaction progress, calcium chloride is added to the reaction bath as necessary to main a weight percent of 70% of the combined weights of both the calcium chloride and the sodium chloride. The following reaction explains the process:

\[
\text{RE}_n\text{O}_m + m\text{CaCl}_2 + 2m\text{Na} \rightarrow n\text{RE} + m\text{CaO} + 2m\text{NaCl}
\]

The "n" and "m" quantities are the number of moles of constituent and the relation of n and m is determined by the oxidation start of the rare earth metal. When the reaction is complete and the stirring has stopped, the reduced metal can be recovered in a clean layer from the bottom of the reaction vessel\(^8\).

**Reduction of Anhydrous Rare Earth Halides:** The second method for the production of rare earth metals is through the reduction of their halides. This reduction method requires the pre-transformation of the rare earth oxides into either chlorides or fluorides. The rare earth halides are less stable than the rare earth oxides which means that there are more options available for reducing agents.

**Metallothermic Reduction of Rare Earth Chlorides:** Trombe and Mahn performed one of the first metallothermic reductions of rare earth chlorides. They prepared cerium, neodymium and gadolinium by reduction of their trichlorides with magnesium. This reduction produced magnesium – rare earth alloy. The magnesium was subsequently removed through vacuum distillation. A few year after Trombe and Mahn experiment, Keller and Karl prepared cerium metal by reducing cerium dichloride with calcium in dolomite lined steel bombs. A Ca – I booster reaction was also used in this process to achieve a good slag – metal separation. The cerium metal was then vacuum melted to remove the calcium slag. The metal was obtained in 99% yield\(^2\).

Spedding and Daane also developed a technique for producing La, Pr, Nd, and Gd metals that utilized calcium as a reducing agent. The rare earth oxide and calcium reaction was performed in tantalum crucible that was heated above the melting temperature of the metal being reduced. The reduction was also performed in a vacuum or inert atmosphere. The metal was obtained in 99% yield\(^9\).
Lithium and sodium have also been used as reducing agent for rare earth chlorides. Block and Campbell were able to prepare high purity yttrium by utilizing both elements as reducing agents. In one technique, the chloride and lithium were placed in a molybdenum crucible and heated to 850 – 900 °C. The reaction took place in an inert atmosphere for four to five hours. The excess lithium and lithium chloride was removed through vacuum distillation. The metal was obtained in 95 – 99% yield\(^2\). In another technique, sodium is distilled into an yttrium chloride crucible. The reaction took place at 800 – 850 °C for 5 -7 hours. The sodium chloride slag was then poured off and any excess sodium was removed through distillation. Only 61 to 85 % of the metal could be recovered through this process\(^6\).

More recent metallothermic studies have focused on lithium vapor reduction of rare earth trichlorides. Nolting, Simons and Klingenberg have used lithium vapor reduction of rare earth trichlorides to prepare yttrium and other rare earth metals that have high melting temperatures. This process involves reducing yttrium trichloride with lithium vapor inside a sealed stainless steel chamber. This reduction produces a lithium chloride slag, which is then distilled away from remaining yttrium crystals. The metal crystals are consolidated through the arc melting process\(^10\).

**Metallothermic Reduction of Rare Earth Fluorides:** Metallothermic reduction of rare earth fluorides have also been studied but these processes were developed much later than processes involving rare earth chlorides and not used as often as rare earth chloride reduction.

In the early 1950's, Gray performed experiments in which rare earth fluorides were reduced with lithium inside a steel bomb. Iodine was added to the reaction to lower the slag melting point and the mixture was heated to 1220 °C. Cerium, lanthanum and neodymium were all successfully recovered from this method\(^11\). Soon after Gray's method was tested, Daane and Spedding developed a very successful technique for reducing rare earth fluorides. In this process, calcium is used as the reducing agent. Calcium and the rare earth fluoride are heated in an argon atmosphere at very temperatures. This process resulted in good metal – slag separation and the slag could be removed from the metal through vacuum melting. This method is very similar to what was adopted for industrial practice\(^7\).

**Reduction through Molten Salt Electrolysis:** Molten salt electrolysis is also a viable option for the production of rare earth metals. Electrolytic methods are typically less complex and expensive than metallothermic reduction methods. This type of process is not completely limited by considerations of chemical stability. Instead, electrolytic methods rely on the theoretical decomposition potential to determine feasibility.

**Molten Salt Electrolysis of Rare Earth Chloride Mixtures:** Lanthanum, cerium, praseodymium and didymium (alloy of neodymium) have been produced by fused salt electrolysis of chlorides on a commercial scale. The maximum operating temperature
of a chloride electrolysis cell is 1100 °C because at higher temperatures the volatility of the electrolyte constituents, resulting is severe attack of the cell wall material by rare earth metals. Lanthanum, cerium, praseodymium and didymium have been successfully recovered through chloride electrolysis because all of these elements have melting points less than 1100 °C. Rare earth elements with high melting temperatures, such as gadolinium, dysprosium and yttrium, have been recovered in limited quantities by fused salt electrolysis of their fluorides rather than their chlorides.\textsuperscript{12}

The technique for fused salt electrolysis of chlorides that was adopted in industry uses an iron or carbon cathode and a graphite anode. The cathode is either the cell container itself or carbon or ions block at the bottom of the cell. The electrolysis takes place in a ceramic, iron, carbon or graphite lined reactor. The electrolyte contains the rare earth chloride and NaCl, KCl, BaCl\(_2\) or CaCl\(_2\). The electrolyte bath is typically heated between 800 – 900 °C. Lanthanum, cerium and didymium metals of 99% or greater purity have been produced by this method.\textsuperscript{12}

The current efficiencies of these cells were usually between 45 – 50%. The current efficiencies in these cells are influenced by various factors. At the cell operating temperature (typically 900°C), the rare earth metals can react with O\(_2\), H\(_2\), CO\(_2\) or graphite forming products that have high melting points and low electrical conductivity, thus decreasing the current efficiency. The presence of oxychlorides can also decrease the current efficiency. Oxychlorides have high melting points than the rare earth chlorides and have limited solubility in the electrolyte. Their presence in the melt increases the viscosity causing current losses due to the lower mobility of the ions in solutions and high operating temperatures.\textsuperscript{6}

**Molten Salt Electrolysis of Rare Earth Oxide-Fluoride Mixtures:** Molten salt electrolysis of rare earth oxide-fluoride mixtures is typically used to produce rare earth metals with high melting temperatures. The first successful technique for producing metal through oxide-fluoride electrolysis was developed by Gray in the early 1950’s. The process utilized a graphite anode and molybdenum cathode. A rare earth oxide was dissolved in a \(\text{REF}_3 - \text{LiF} - \text{BaF}_2\) electrolyte and the mixture was externally heated in a carbon reactor. The reaction also took place in an argon gas atmosphere and an inert crucible was placed below the cathode to recover the rare earth metal.

During the 1960’s, much of the research and development of oxide-fluoride electrolysis was carried out by the Reno Metallurgy Center of the United States Bureau of Mines. An important feature of the electrolytic cells that were developed at Reno was that there was layer of frozen bath on the interior surface of the graphite reactor. This layer was called a skull and kept the rare earth metals from coming in contact with the graphite crucible. The cells were first used to recovery cerium metal. During electrolysis, cerium nodules formed on the surface of the skull. After the procedure was complete and the cell was cooled to room temperature, the skull was taken into
open air and broken up to recover the cerium nodules. This technique was also used to recover neodymium, praseodymium and didymium. The current efficiencies for these cells typically ranged from 75-95%. The electrolyte consisted of the RE₂O₃, REF, LiF, and BaF₂. Rare earth metals could be produced in 99% or greater purity through this method¹².

Summary

Very small amount of rare-earth metals is produced outside China. Several methods have been studied on a laboratory scale as well as some on the pilot level in other countries. The high thermodynamic stability of rare-earth oxides as well as halides makes the metal production challenging. Metallothermic reduction of oxides has shown better potential for RE production than reduction of halides or processes based on electroreduction.

References

CHINA’S RARE EARTH ORE DEPOSITS AND BENEFICIATION TECHNIQUES

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Abstract

China possesses the largest resource of rare earth elements (REE) in the world and the reserve of REE in China takes up over 40% of the total global reserve. China has dominated the world REE production since 1980s. Bayan Obo REE-Nb-Fe deposit situated in Inner Mongolia is the world’s largest known REE ore deposit with the reserve of 48 Mt REO and the largest REE production resource. Other two major in production REE deposits are Mianning REE deposit in Sichuan and Weishan REE deposit in Shandong. The weathered crust elution –deposited REE ore (ion adsorption REE deposit), as the world unique REE deposit found in China, is currently the second largest REE production resource containing high contents of heavy REE. In the paper, the ore properties of these REE deposits are introduced and the renovation and progress on the beneficiation techniques including flowsheets, flotation and leaching reagents and technological indexes on these ores are discussed.

Introduction

China has the largest resource of rare earth elements (REE) in the world. According to Mineral Commodity Summaries in 2001 the reserves and reserve bases of REE in the world in 2000 are shown in Table 1. It is indicated that the reserve of REE in China takes up over 40% of the world reserve. The newest Mineral Commodity Summaries 2014 shows the similar results.

The resources of rare earth elements (REE) in China are mainly divided into four types of deposits which consist of 95% total REE resources of China. They are the Bayan Obo REE–Fe–Nb Ore Deposit in Inner Mongolia, the Mianning REE Ore Deposit in Sichuan Province, the Weishan REE Ore Deposit in Shandong Province and the Weathered Crust Elution–deposited Rare Earth Ore (The Ion Adsorption Type Rare Earth Ore)
mainly in Jianxi Province, but also distributed in Guandong, Fujian and Guanxi Provinces.

**Table 1:** the reserves and reserve bases of REE in the world in 2000 (REO, 10^4 t)

<table>
<thead>
<tr>
<th>Country</th>
<th>Reserve</th>
<th>Reserve base</th>
<th>%</th>
<th>Country</th>
<th>Reserve</th>
<th>Reserve base</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>4300</td>
<td>4800</td>
<td>43</td>
<td>South Africa</td>
<td>39</td>
<td>40</td>
<td>0.4</td>
</tr>
<tr>
<td>Russia</td>
<td>1900</td>
<td>2100</td>
<td>19</td>
<td>Brazil</td>
<td>28</td>
<td>31</td>
<td>0.3</td>
</tr>
<tr>
<td>USA</td>
<td>1300</td>
<td>1400</td>
<td>13</td>
<td>Malaysia</td>
<td>3.0</td>
<td>3.5</td>
<td>0</td>
</tr>
<tr>
<td>Australia</td>
<td>520</td>
<td>580</td>
<td>5.2</td>
<td>Sri Lanka</td>
<td>1.2</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>India</td>
<td>110</td>
<td>130</td>
<td>1.1</td>
<td>Other</td>
<td>1704.8</td>
<td>1814.2</td>
<td>17</td>
</tr>
<tr>
<td>Canada</td>
<td>94</td>
<td>100</td>
<td>0.9</td>
<td>Total</td>
<td>10000</td>
<td>11000</td>
<td>100</td>
</tr>
</tbody>
</table>

The distributions of REE in the China's REE ore deposits are shown in Table 2. It is observed that high percentages of three main light rare earth elements La, Ce and Nd are found in Bayan Obo REE–Fe–Nb Ore Deposit, Sichuan Mianning REE Ore Deposit and Shandong Weishan REE Ore Deposit. However, in the Ion Adsorption Type Rare Earth Ore (especially type B) high contents of Y and other heavy REE are contained.

**Table 2:** the distributions of REE in the China’s REE ore deposits

<table>
<thead>
<tr>
<th>Content of REO</th>
<th>Bayan Obo REE–Fe–Nb Ore</th>
<th>Sichuan Mianning REE</th>
<th>Shandong Weishan REE</th>
<th>Ion Adsorption Type Rare Earth Ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₂O₃</td>
<td>24 – 26</td>
<td>28 – 30</td>
<td>32</td>
<td>Type A: 31 – 40</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>50</td>
<td>45 – 50</td>
<td>48 – 50</td>
<td>Type A: 3 – 7</td>
</tr>
<tr>
<td>Pr₆O₁₁</td>
<td>3 – 5</td>
<td>5</td>
<td>4</td>
<td>Type A: 7 – 11</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>16 – 18</td>
<td>12 – 14</td>
<td>11 – 12</td>
<td>Type A: 26 – 35</td>
</tr>
<tr>
<td>Sm₂O₃</td>
<td>1.5</td>
<td>1.5 – 2</td>
<td>1.0 – 1.8</td>
<td>Type A: 4 – 6</td>
</tr>
<tr>
<td>Eu₂O₃</td>
<td>0.2</td>
<td>0.4</td>
<td>0.1 – 0.2</td>
<td>Type A: 0.5</td>
</tr>
<tr>
<td>Gd₂O₃</td>
<td>0.4</td>
<td>0.8 – 1.0</td>
<td>0.3 – 0.5</td>
<td>Type A: 4</td>
</tr>
<tr>
<td>(Tb – Lu)₂O₃</td>
<td>0.2 – 0.3</td>
<td>1</td>
<td>0.4 – 0.6</td>
<td>Type A: 4 – 5</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>0.3</td>
<td>0.76</td>
<td>0.1 – 0.3</td>
<td>Type A: 9 – 11</td>
</tr>
</tbody>
</table>

The Bayan Obo REE–Fe–Nb Ore Deposit

**Mineralogy**

The Bayan Obo REE-Nb-Fe deposit is situated in Inner Mongolia on the northern edge of the North China Kraton, 135 km northwest of Baotou (110°E, 41°47′N). It is a giant polymetallic rare earth element (REE)-Fe-Nb ore deposit of hydrothermal origin. It was first discovered as a Fe deposit by Prof. Ding Daoheng in 1927. The estimated total reserves of Fe (average grade Fe 35 wt%), Nb (average grade of 0.13 wt%) and REE (average grade REO 6 wt%) are 1.5 Bt, 1 Mt and 48 Mt. It is the world's largest known REE ore deposit. The Bayan Obo mining area is shown in Figure 1.
The ore composition in the Bayan Obo is very complex, 71 elements and 170 minerals are found, one element could exist in several or more than ten different minerals, mineral symbiosis relationship is close and complicated, and dissemination size is fine. More than 90% rare earth elements in ore are existed in independent minerals, and about 4% ~ 7% of REE dispersed in iron minerals and fluorite. Total 15 kinds of rare earth minerals are found but the principal ones are bastnaesite [(Ce,La,Nd)(CO₃)F] and monazite [(Ce,La,Nd)PO₄] with the ratio of 7:3 or 6:4, whereas magnetite and hematite are the dominant Fe-ore minerals. Meanwhile, several kinds of niobium minerals are contained in the ore such as columbite (FeNb₂O₆), aeschynite ((Y,Ca,Fe)(Ti,Nb)₂(O,OH)₆) and fersmite ((Ca,Ce,Na)(Nb,Ta,Ti)₂(O,OH,F)₆) etc. The main gangue minerals are quartz, apatite, dolomite and fluorite etc. These minerals consist of both primary and secondary metamorphic minerals of the host rocks and the epigenetic ore and gangue minerals introduced by hydrothermal solutions. The minerals of the Bayan Obo ore deposit are listed in Table 3.

Most of the Bayan Obo minerals, particularly in the banded ore, are very fine to extremely fine grained. Most Fe–REE–Nb minerals are closely associated with fine grain sizes. The grain sizes of REE minerals are in the range of 0.01 – 0.074 mm and the amount of less than 0.04 mm is accounted for 70% ~ 80%.
Table 3: principal minerals of the Bayan Obo deposit

<table>
<thead>
<tr>
<th>Mineral category</th>
<th>Principal minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Host rock minerals</td>
<td>ferroan dolomite, Sr- and Mn-calcite, quartz, illite, bòtite, apatite, alite</td>
</tr>
<tr>
<td>REE ore minerals</td>
<td>monazite, (Ca,La,Nd)(PO₄)₃F, bastnaesite, (Ce,La,Nd)(CO₃)₃F, hauyneite, Ba((Ce,La,Nd)(CO₃)₃F, partite, (Ca,La,Nd)(CaCO₃)₃F, cebraste, Ba₅Ce₂(CO₃)₃F₂, Cs₅</td>
</tr>
<tr>
<td>Nb (± REE) minerals</td>
<td>columbite, Fe₃NbO₅, aeschynite, (Ce₂,Ca₂,Fe₂,Th₂)(T₄N₂O₁₂)O₂, fergusonite, Y₂(NO₃)₆, fersmite, (Ca,Ca,Na)(Nb,Ti)₂(O₂OH)₆, pyrochlore, (Ca,Na₂)₂Nb₂O₆(O₂OH)₆, Nb₂O₅</td>
</tr>
<tr>
<td>Fe ore minerals</td>
<td>magnetite, hematite, martite, goethite, ilmenite</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral category</th>
<th>Principal minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Other carbonate minerals</td>
<td>benstonite, (Ca,Sr)ₓBaᵧMg(CO₃)ₓ</td>
</tr>
<tr>
<td>Common gangue and other minerals</td>
<td>fluorite, barite, aegirine, magnetio-ardevedonite, magnetio-rebeckite, apatite, phlogopite, microcline, albite, bafiite, Ba(Fe₂,Mnₓ)₂Ti₃O₈(O₂OH)₆, cerianite, (Ce,Th)O₂</td>
</tr>
<tr>
<td>Sulfide gangue minerals</td>
<td>pyrite, pyrrhotite, sphalerite, galena, chalcopyrite</td>
</tr>
</tbody>
</table>

Beneficiation techniques

Compared with domestic and abroad single bastnaesite ores, the Bayan Obo ores are much more difficult to upgrade due to its similar physical and chemical properties with iron minerals and gangue minerals associated closely, a lot of experimental studies by many research institutes in China on the rational exploitation of the Bayan Obo REE deposits had been conducted since the late 1950s and more than 20 beneficiation techniques have been reported. A significant progress on REE minerals processing had been made in the early 1990s and the mixed and separate REE concentrates with high-grade and high recovery were obtained from the iron ores.

The flowsheet of low intensity magnetic separation (LIMS) – high intensity magnetic separation (HIMS) – flotation (Figure 2) was considered the most successful one to be used in industrial plants which was developed by Changsha Metallurgical Research Institute in 1990.

As shown in Figure 2, after crushing the ore is ground to 90 – 95% passing 0.074 mm. By LIMS (routher and cleaner) magnetite is recovered in the LIMS concentrate. The tailings of LIMS is processed through HIMS rougher at the magnetic field strength of 1.4T to recover another Fe mineral hematite and most REE minerals. And hematite and REE minerals contained in the HIMS rougher concentrate are separated by HIMS cleaner at the magnetic field strength of 0.6T. Combined LIMS and HIMS concentrates reported to the Fe reverse flotation to get the final Fe concentrate and the HIMS cleaner tailings containing most REE minerals is processed by flotation to get REE concentrates.

At the REE flotation circuit, the feed grade of REO is 9.78 – 12% (HIMS cleaner tailings). The flotation is performed at low alkaline condition (pH9) and the flotation reagents
contained naphthyl hydroxamic acid as the collector of REE minerals, sodium silicate as the depressant of silicates and J10 as the frother. The feed solids is 35-45% wt. One stage of rougher flotation, plus one scavenger flotation and two cleaner flotation stages produced an REO concentrate at a grade of 55% and a secondary REO concentrate at a grade of 34% with the combined recovery of 72~75%. However, these concentrates are the mixture of REE minerals mainly bastnaesite and monazite. The separation of bastnaesite and monazite has been reached by further flotation using phthalic acid or Benzoic acid as the collector of bastnaesite and alum as the depressant of monazite.

**Figure 2:** beneficiation flowsheet of the Bayan Obo deposit ore

Different flotation reagents had been tested. Only a rare earth concentrate with grade 15%~20% and the low recovery could be gotten by using fatty acids, such as oxidized paraffin and oleic acid, as the collector in rare earth mineral processing in earliest. C5 ~ 9 hydroxamic acid by saponification was primarily used for rare earth mineral flotation from 1970s and 1980s, then the cyclic alkyl hydroxamic acid synthesized by naphthenic acid was used as collector because the synthesis materials of fatty acids C5 ~ 9 in short supply. A miracle result of up to 60% REO flotation concentrate was obtained by processing previous concentrate of REO 25% ~ 30% from gravity separation concentrator when the major adjustments of the compatible depressants were made. In 1976, the plant test was succeeded, and the commercial production began in 1978. By application of the reagents system, the rare earth concentrate of REO> 60%, flotation recoveries of 60% to 65% were obtained. Since then, high-grade commercial rare earth concentrates were produced. Because the selectivity of cyclic alkyl hydroxamic acid and alkyl hydroxamic acids was found poor the collector of H205, as the representative of aromatic hydroxamic acid, was successfully developed in 1986 by using naphthalene as raw material through
sulfonated - hydrolysis - alkali fusion hydroxylation for preparation of intermediates naphthol, and then acylation reaction and condensation system with hydroxylamine (-NH-OH), to make naphthyl isobutyl group hydroxamic acid. The rare earth grade and recovery could significantly be improved by using new generation of rare earth mineral collector H205 with only water glass and the activator sodium fluoride in the flotation process was not needed. After the 1990s, a hydroxamic acid with dual activating group, the No.8 flotation oil, improved from H205, has been used in the Bayan Obo rare earth plant as a collector.

By the end of 2012, the Bayan Obo rare earth flotation concentrator had been developed into an annual output of 250,000 t of REE concentrates (contained 50% REO).

**The Sichuan Mianning REE Deposit**

Mineralogy

The Sichuan Mianning REE Ore Deposit was found between 1985–1986. It is an alkaline pegmatite carbonate type rare earth deposit. The industrial reserve is $1 \times 10^6$ t with the average grade of REO 3.7%. It is rich in light REE and heavy REE as well such as europium, yttrium etc. The chemical analysis results are shown in Table 4.

Bastnaesite is the main rare earth mineral and chevkinite and parisite are found in the ore. Other associated minerals are barite (BaSO₄), fluorite (CaF₂), iron and manganese minerals and small amount of galena. The ore is divided into granule and powder types. The granule ore has coarse grain size usually >1 mm. The grain size of bastnaesite is between 1 to 5 mm. The powder ore is the weathered product of original ore and takes up about 20% of total ore weight. The grade is about REO 3–7% and the grain size is 80% passing 325 mesh.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
<th>Element</th>
<th>Wt %</th>
<th>Element</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>REO</td>
<td>3.70</td>
<td>F</td>
<td>5.50</td>
<td>Na₂O</td>
<td>1.39</td>
</tr>
<tr>
<td>TFe</td>
<td>1.12</td>
<td>CaO</td>
<td>9.62</td>
<td>MnO</td>
<td>0.73</td>
</tr>
<tr>
<td>SiO₂</td>
<td>31.00</td>
<td>MgO</td>
<td>1.10</td>
<td>BaO</td>
<td>21.97</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.17</td>
<td>S</td>
<td>5.33</td>
<td>K₂O</td>
<td>1.31</td>
</tr>
<tr>
<td>FeO</td>
<td>0.43</td>
<td>P</td>
<td>0.24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Beneficiation techniques**

Three types of flowsheets are industrially used: the gravity concentration flowsheet, the magnetic – gravity concentration flowsheet and the gravity – flotation flowsheet.
The coexistence of massive and powdered black sludge, Fe-Mn weathered amorphous aggregates slime greatly influences the floatability of REE minerals.

Gravity separation
The ore was ground to 62% passing 200 mesh and hydro classified into the four size fractions. The shaking tables were used to process the fractions separately. Three different grade bastnaesite concentrates were obtained with the grades of 30%, 50% and 60%. The overall recovery was 75%.

Magnetic –gravity separation
After grinding the ore was concentrated by LIMS and HIMS separation and the magnetic concentrate with the grade of 5.64% was obtained. The recovery of magnetic circuit was 74.2% and yield 42%. And then the magnetic concentrate was classified into four size fractions and processed separately by shaking tables. The final concentrate with the grade of REO 52.3% was obtained. The overall recovery of RE was around 55%.

Gravity separation-flotation
As shown in Figure 3 the ore was primarily ground to 50% passing 200 mesh and hydro classified into four size fractions. The classified fractions were concentrated by the shaking tables separately. The grade of overall gravity concentrate was REO 30% with the RE recovery of 74.5%. The gravity concentrate was reground to 70% passing 200 mesh for flotation. C5−9 hydroximic acid (H205) and phthalate in the ratio of 1:1, sodium carbonate, sodium silicate were used as the flotation reagents at pH8-9. By one rougher, one cleaner and one scavenger flotation the concentrate with the grade of REO 50–60% was acquired at the RE recovery of 50–60%.
**The Shandong Weishan REE Deposit**

**Mineralogy**

The ore deposit was first found in 1958 and the exploration was finished in 1975. The reserve of RE was about $2.55\times10^6$ t and the average geological grade was 3.13%. It is a quartz–barite–carbonate type RE ore deposit. The main RE minerals are bastnaesite and parsite and the main associated minerals are barite, calcite, quartz and fluorite etc. The grain sizes of RE minerals are coarse in the range of 0.04–0.5 mm. The chemical compositions are shown in Table 5.

### Table 5: Chemical compositions of Shandong Weishan REE Ore

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
<th>Element</th>
<th>Wt %</th>
<th>Element</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>REO</td>
<td>3.71</td>
<td>F</td>
<td>0.698</td>
<td>Na$_2$O</td>
<td>3.53</td>
</tr>
<tr>
<td>TFe</td>
<td>2.81</td>
<td>CaO</td>
<td>1.18</td>
<td>Th</td>
<td>0.002</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>47.92</td>
<td>MgO</td>
<td>1.18</td>
<td>BaO</td>
<td>11.99</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>22.48</td>
<td>S</td>
<td>2.1</td>
<td>K$_2$O</td>
<td>1.85</td>
</tr>
</tbody>
</table>

**Beneficiation techniques**

The Weishan REE flotation plant was built in 1982. The ore was ground to 65–75% passing 200 mesh and REE minerals were floated with once rougher, three scavengers and three cleaners. In 1980s oleic acid and kerosene were used as the collectors of RE minerals at acidic condition of pH 5 using sulfuric acid. After 1991 with the ore grade dropped to 3–4%, a specific collector with formula C$_6$H$_4$OHCONHOH was used with the addition of sodium silicate and frother L$_{101}$. The flotation was run at the weak alkaline condition of pH 8–8.5. The RE concentrate with the grade of REO >60% at the recovery of 60–70% was obtained. Meanwhile, a secondary RE concentrate with the grade of REO 32% at the recovery of 10–15% was acquired. According to market demand, REE concentrate with the grade of 45–50% REO at the recovery of 80–85% has been produced and barite has also been recovered by flotation from REE flotation tailings.

**The Weathered Crust Elution-deposited REE Ore (The Ion Adsorption REE Deposit)**

**Mineralogy**

China’s weathered crust elution–deposit rare earth ore or called ion adsorption rare earth ore is the unique REE deposit in the world. It was found in 1969 in Jianxi Province containing two types of this deposit, light REE type and heavy REE type, and was also found in other provinces Fujian, Hunan, Guandong and Guanxi. The known reserve of
weathered crust elution–deposit rare earth ore in China is over $1 \times 10^6$ t (REO) and the heavy RE reserve in China occupies over 80% of the world total heavy REE reserve. Now China produces about $1 \times 10^6$ t concentrate (REO >60%) from this ore annually.

The deposit was considered to form by many years weathering of granite and effusive rocks. It has the characteristics of shallow ore body coverage, soft ore and very fine grain size. The 80% –90% REE in the state of positive hydrated ions are adsorbed on the surface of clay minerals such as kaolinite, halloysite and illite. The ore is relatively low-grade, generally only 0.05% to 0.5% REO, with high heavy REE.

**Extraction Techniques**

Because the REE in the ore mainly occur in the state of hydrated ions adsorbing on the surface of clay minerals they can’t be effectively concentrated by conventionally physical methods but extracted by the ion–exchange method. The adsorbed REE ions are not dissolved in water or ethyl alcohol but they are dissolved in the electrolytes solutions of NaCl, (NH₄)₂SO₄ and NH₄Cl by ion–exchange. The percentages of REE in different phases are shown in Table 6. It is indicated that over 80% REE are ion exchangeable.

**Table 6: REE concentration in different phases (% mass fraction)**

<table>
<thead>
<tr>
<th>Rare Earth</th>
<th>Aqueous</th>
<th>Ion Exchangeable</th>
<th>Colloidal</th>
<th>Sediment</th>
<th>Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>LN</td>
<td>6.15×10⁻³</td>
<td>80.62</td>
<td>5.30</td>
<td>13.36</td>
<td></td>
</tr>
<tr>
<td>XF</td>
<td>8.14×10⁻³</td>
<td>83.58</td>
<td>3.23</td>
<td>12.63</td>
<td></td>
</tr>
<tr>
<td>NH</td>
<td>1.47×10⁻³</td>
<td>84.94</td>
<td>4.98</td>
<td>9.09</td>
<td></td>
</tr>
</tbody>
</table>

In 1970s as a major extraction method NaCl was used as the leaching solvent to dissolve REE by ion exchange. But high solvent concentration and long leaching time were required. And the solvent consumption and processing cost were high. Meanwhile, the grade of RE concentrate can only reach 70% REO. Since 1980s (NH₄)₂SO₄ has been used to replace NaCl as the solvent. A high grade (REO 92%) of RE concentrate has been achieved.

The process is usually run in a cement bath with the volume of about 10–20 m³. When the bath is filled with the ore to the height of about 1.5 m the solvent of (NH₄)₂SO₄ solution with the concentration of 1~4% is poured through the ore for leaching. The pregnant solvent is obtained at the bottom of the bath. Oxalic acid is used as the precipitant to get mid product of oxalic acid–rare earths and further processed by burning to get final rare earths product (>REO 92%). Ammonium bicarbonate also has been used as a competitive precipitant. The flowsheet of the extraction technique is shown in Figure 4.
Figure 4: REE extraction technique for weathered crust elution–deposit REE ore

The in-situ leaching process also called the solution mining was studied from 1980s to resolve the ecological environmental problems in the exploitation by the bath leaching technology. The wells are drilled in the natural orebody and the leaching regent is injected. REE ions were selectively leached. Collected leachate is precipitated by the solution of oxalic acid or ammonium bicarbonate to obtain rare earth oxide products. The water is recycled. It was reported that two key technical problems must be solved during the in-situ leaching process. One is how to avoid the leaching reagent solution spreading around the wells to cause the environmental pollution and the other is how to recover the leachate so as optimize the leaching rate. The technology has been utilized in Wenfeng, Jiangxi province. More than 200 t of REE are extracted annually at the REE recovery of 70%.

Conclusions

China possesses the largest resource of rare earth elements (REE) in the world and has dominated the world REE production since 1980s. The resources of rare REE are mainly divided into four deposits which consist of 95% total REE resources of China. They are the Bayan Obo REE–Fe–Nb Ore Deposit, the Sichuan Mianning REE Ore
Deposit, the Shandong Weishan REE Ore Deposit and the Weathered Crust Elution–deposited Rare Earth Ore.

The Bayan Obo REE-Nb-Fe deposit situated in Inner Mongolia on the northern edge of the North China is a giant polymetallic rare earth element (REE)-Fe-Nb ore deposit of hydrothermal origin. It is the world's largest known REE ore deposit with REO 48 Mt with average grade REO 6 wt%. The ore composition in the Bayan Obo was very complex and the principal REE minerals are bastnaesite and monazite. Most Fe–REE–Nb minerals are closely associated with fine grain sizes. The flowsheet of low intensity magnetic separation (LIMS) – high intensity magnetic separation (HIMS) – flotation was considered the most successful one to be used in industrial plants which was developed in 1990s.

The Sichuan Mianning REE Ore Deposit was found between 1985 – 1986. It is an alkaline pegmatite carbonate type rare earth deposit. The industrial reserve is 1×10⁶ t with the average grade of REO 3.7%. Bastnaesite is the main rare earth mineral. Three processes have been used industrially, magnetic – gravity separation process, gravity separation process and gravity separation – flotation process.

The Shandong Weishan REE Deposit was first found in 1958 and the exploration was finished in 1975. The reserve of RE was about 2.55×10⁶ t and the average geological grade of 3.13%. It is a quartz–barite–carbonate type RE ore deposit. The main RE minerals are bastnaesite and parasite. The flotation plant was built in 1982.

Chinese weathered crust elution–deposit rare earth ore or called ion adsorption rare earth ore is the unique REE deposit in the world. The 80% –90% REE in the state of positive hydrated ions are adsorbed on the surface of clay minerals which can't be effectively concentrated by conventionally physical methods and usually are extracted by the ion–exchange method using NaCl, (NH₄)₂SO₄ or NH₄Cl as leaching solvents. The process is usually run in a cement bath and the in-situ leaching process has been also used.

References
5. Jörg Neßler, Giant Bayan Obo REE-Fe-Nb Ore Deposit of Inner Mongolia, China, January 2007
ECONOMICS OF RARE EARTHS: THE BALANCE PROBLEM

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Abstract

The balance between the demand by the economic markets and the natural abundance of the REEs in ores is a major problem for manufacturers of these elements. This is the so-called Balance Problem (or Balancing Problem). The ideal situation is a perfect match between the demand and production of REEs, so that there are no surpluses of any of the REEs. The Balance Problem implicates that the rare earth industry has to find new applications for REEs that are available in excess, or to search for substitutions for REEs that have limited availability and that are high in demand. Different solutions are proposed to solve the Balance Problem: diversification of REE resources, recycling, substitution, reduced use and new high-volume applications. It is shown that the issue of thorium in REE ores is related to the Balance Problem.

Introduction

The global annual production of rare earths or rare-earth elements (REEs) is typically expressed in tonnes of rare-earth oxides (REOs). At present, the estimated yearly total production of REOs is about 125,000 tonnes, although accurate production numbers are very difficult, if not impossible, to find. However, these total production numbers do not tell anything about the availability of the individual REEs. First of all, not the total amount of REE ores mined is of importance, but rather the total amount of REE concentrate separated in the different individual REEs. For some applications, such as mischmetal, no separated REEs are required. Secondly, the REEs are not present in equal amounts in the REE ores, due to differences in the natural abundances of these elements. The general trend in the natural abundance of the rare earths is that the elements become scarcer with increasing atomic number Z; as the abundances decrease over the lanthanide series, the heavy rare-earth elements (HREEs) are much less abundant than the light rare-earth elements (LREEs).¹ Moreover, elements with an even atomic number Z are more abundant than elements with an odd atomic number (Oddo-Harkins rule). For example, cerium (Z = 58) is more abundant with respect to its neighbours lanthanum (Z = 57) and praseodymium (Z = 59). Cerium is the dominating REE in LREE-rich ores (bastnäsite and monazite), while yttrium is the main REE in HREE-rich ores (xenotime and ion-adsorption ores).
The availability of the individual REEs is of concern for applications that require the use of pure REEs, such as lamp phosphors and permanent magnets. If the REEs that are required for high-volume applications have a low natural abundance, the minimum quantity of REE concentrate that needs to be processed and separated is that quantity that will produce at least the amount of REEs required for the critical applications. As a consequence, some REEs will be produced in larger quantities than required by the REE market and, subsequently, these need to be stockpiled. The balance between the demand by the economic markets and the natural abundances of the REEs in ores is a major problem for manufacturers of these elements. This is the so-called Balance Problem (or Balancing Problem).\(^2\)\(^3\) The ideal situation is a perfect match between the demand and production of REEs, so that there are no surpluses of any of the REEs. This would result in the lowest market price for any of the REEs, because the production costs are shared by all the elements. Unfortunately, a market in balance is very difficult to achieve, because of changes in demand due to technological evolutions in applications. The result is a sometimes very high demand of a REE that is a minor constituent in the ore (such as dysprosium), while the demand of the major constituent (such as yttrium) is much lower. The size of the REE market is different in value and volume. For instance, lamp phosphors are a very important application of REEs in terms of value (1/3 of the REE market), but they are a rather modest application in terms of volume (about 7%). The Balance Problem is related to the volumes of the individual REEs consumed.

For the REE industry the Balance Problem is a more important issue than the availability of REE resources, not to say that it is the most important issue facing the REE industry. This paper gives an in-depth analysis of the Balance Problem and offers several possible solutions.

**History of the Balance Problem**

The balance problem became an issue when purified REEs were started to be used in applications. Older applications of REEs consumed mixtures of REEs and no separation into pure single elements was required. A good example is mischmetal, which is an alloy of LREEs, with the REEs in the same atomic ratios as they occur in the REE ore minerals. Also for other older applications such as polishing powders or fluid cracking catalysts no pure REEs have to be used. All REEs that were produced could be consumed.

The first application of pure REEs was the use of europium as active component of the red cathodoluminescent phosphors in colour television screens (first \(\text{YVO}_4: \text{Eu}^{3+}\), later \(\text{Y}_2\text{O}_2\text{S}: \text{Eu}^{3+}\)). In the mid-1960s and the early 1970s, europium was the most critical REE
because it has a low natural abundance and it was high in demand for the production of these red phosphors. In that period, nearly all of the global supply of europium was produced from the bastnäsite ore of the Mountain Pass mine in California. In fact, the Mountain Pass mine was in that period mainly operated for the production of europium. The bastnäsite of the Mountain Pass mine is relatively rich in europium (0.1%) compared to monazite (<0.05%). Nevertheless, the low concentrations of europium implied that large surpluses of the LREEs were produced and needed to be stockpiled: to obtain 1 tonne of Eu₂O₃ from bastnäsite, one had to excavate an amount of REE ores that contained 300 tonnes of La₂O₃, 450 tonnes of CeO₂, 38 tonnes of Pr₆O₁₁, 118 tonnes of Nd₂O₃, 7.3 tonnes of Sm₂O₃, 1.4 tonnes of Gd₂O₃ and 0.9 tonnes of Y₂O₃.⁴ It should be mentioned that it is possible to selectively remove europium from mixtures of REEs by reduction of europium(III) to europium(II), for instance by chemical reduction with zinc amalgam or by electrochemical reduction.

In the 1970s and 1980s, samarium was the most critical REE because of its use in samarium-cobalt permanent magnets. At that time, the production of samarium-cobalt magnets was limited by the availability of Sm₂O₃ on the market. At present, the share of samarium-cobalt magnets in the permanent magnet market is less than 2%, and an excess of samarium is being produced. Before 1985, there were no industrial applications for dysprosium, and neodymium metal was not produced on an industrial scale. At that time, it could not be predicted that less than 30 years later, neodymium and dysprosium would be high in demand for neodymium-iron-boron magnets. With respect to holmium, thulium, ytterbium and lutetium no high-volume applications currently exist.

Due to the Balance Problem, there has also been a shift in the types of REE ores used. Until the 1960s, monazite was the main ore (monazite era). However, for a long time the REEs were just a by-product of the production of thorium which was used for the manufacturing of incandescent gas mantles. In the 1960s, bastnäsite became the most important REE ore, with the Mountain Pass mine in California as the main production site (Mountain Pass era). Bastnäsite was ideal to cover the increasing needs of lanthanum and cerium, and as well as to fulfil the demand of europium. Gradually, monazite was favoured again because of its higher content of HREEs and yttrium. The steadily increasing demand of yttrium (mainly for its use in lamp phosphors and yttria-stabilised zirconia) implied that also the yttrium-rich phosphate xenotime was processed as a REE ore. From the end of the 1980s on, the HREE-rich ion-adsorption ores (laterite clays) from southern China became the most important resource for yttrium and the HREEs.
Current market situation and evolution in the future

At present the LREE market is driven by the demand for neodymium for neodymium-iron-boron (NdFeB) magnets.\(^5\) For instance, about 25000 tonnes of neodymium were required for the production of magnets in 2011. This means that sufficient quantities of REE ores had to be mined to produce at least 25000 tonnes of neodymium. Since the natural abundance of neodymium is relatively low in the LREE ores, cerium, praseodymium and samarium are produced in excess, and have to be stockpiled. The lanthanum market is in balance, thanks to its use in nickel metal hydride batteries and optical glasses. A few years ago, it was predicted that there would be a sharp decline in the use of nickel metal hydride batteries due to the increased use of lithium-ion batteries. However, there are still many safety issues related with these lithium-ion batteries; overheating of the organic electrolytes can cause fires. For these reasons, it is likely that nickel metal hydride batteries will continue to be used for several years to come in high-power applications such as electric vehicles. The HREEs are produced in much smaller quantities than the LREEs, so that the Balance Problem is a bigger issue for the LREE market than for the HREE market. At present, the HREE market is driven by the demand for dysprosium, which is used to increase to high-temperature performance and resistance to demagnetisation (i.e. the intrinsic coercivity) of NdFeB magnets. About 1600 tonnes of dysprosium were consumed in 2011. The supply equals the demand for europium, yttrium and erbium. There is a shortage of terbium, but this problem can still be solved by the use of stockpiles. Gadolinium, holmium, thulium, ytterbium and lutetium are produced in excess and are stockpiled. This stockpiling is not a major issue in terms of volumes, but it causes a loss of potential profit for the REE producers.

The REE market is a rapidly changing market. New applications as well as the sudden disappearance of well-established applications could bring the REE market out of balance. Although the present REE market is driven by the demand for neodymium and dysprosium, this could rapidly change, as shown by the historical evolutions in the REE markets. Although there is currently an oversupply of gadolinium, this global excess could turn into a shortage if magnetic refrigerators would be mass-produced. However, it must be admitted that present research activities in the field of magnetic refrigerators are focusing on the development of REE-free materials with a large magnetocaloric effect. Given the fact that kilogramme quantities of gadolinium are required for the construction of one magnetic refrigerator, it is not realistic to assume that such devices would be mass-produced; there is simply not enough gadolinium available on the world to achieve this goal.

It is very likely that within the next years a dramatic change will occur in the lamp phosphor market that will cause an imbalance of the HREE market. At present,
europium, terbium and yttrium are considered as three of the five most critical rare earths (the other two being neodymium and dysprosium) because of their use in the red lamp phosphor Y₂O₃:Eu³⁺ (YOX), the green lamp phosphors LaPO₄:Ce³⁺,Tb³⁺ (LAP), (Gd,Mg)Ba₂O₁₂:Ce³⁺,Tb³⁺ (CBT), (Ce,Tb)MgAl₁₁O₁₉ (CAT) and the blue phosphor BaMgAl₁₀O₁₇:Eu²⁺ (BAM) in fluorescent lamps and compact fluorescent lamps (energy-saving lamps). Nevertheless, the fluorescent lamps market is rapidly shrinking due to the increasing success of the light-emitting diodes (LEDs). Many types of LEDs do not contain rare earths at all; they produce white light by a combination of red, green and blue LEDs standing in close proximity to each other, similarly to the red-green-blue pixels in old-fashioned cathode-ray tubes. This change from fluorescent lamps to LEDs will make the conventional lamp phosphors largely obsolete, although they could still find use in some niche applications. As a consequence, one may expect an oversupply of europium. The lamp phosphor Y₂O₃:Eu³⁺ is by far the most important application of europium. Smaller quantities of luminescent europium compounds are used in safety markers, for instance in the luminescent inks of EURO banknotes. Considering that no other high-volume applications of europium are close to market introduction, europium will no longer be a critical element in the years to come. An oversupply of europium is less of an issue than an oversupply of cerium, since the global production volumes of europium are much smaller than those of cerium. For terbium, it is much easier to find alternative applications. Terbium can substitute for dysprosium in NdFeB permanent magnets (vide infra). Also for yttrium other applications than lamp phosphors are possible, since yttrium is a very useful element for the preparation of high-tech ceramic materials, for instance, yttria-stabilised zirconia.

**How to solve the Balance Problem?**

Increasing the overall REE production to meet the highest demand of any REE and to stockpile the other REEs with lower demand, seems to be an obvious solution for the Balance Problem. However, this will increase the overall price of the REEs, due to the extra costs for separating the REE mixtures and stockpiling the REEs produced in excess of the demand. Adjusting the overall REE production to optimise the REE producer’s operational margins will create surpluses of some REEs and shortages of other REEs. Shortages of a minor constituent lead to dramatic price increases of this REE due to its (very) high price inelasticity. Preferentially, the REE market is driven by the demand for elements that are very abundant (cerium and lanthanum), since this will create less problems with stockpiling of the elements that are available in excess. The unbalanced use of a single REE in a high volume application has to be avoided, especially if this element has a low natural abundance, because this will cause a serious imbalance of the market. There are different solutions that can help to alleviate the Balance Problem. These will be discussed each in some detail. Since the REE markets are rapidly changing, it is extremely difficult to extrapolate the future demand of individual REEs
on the basis of data for the present demand of these elements. Long-term predictions (for 25 or more years) should be interpreted with caution.\textsuperscript{7}

**Solution 1: Diversification of REE resources**

At present, the global REE supply is produced from a limited number of ore types: bastnäsite, monazite, xenotime and ion-adsorption clays. Bastnäsite and monazite are rich in LREEs, whereas xenotime and ion-adsorption ores are rich in HREEs and yttrium. The composition of these ores can show some variation from deposit to deposit, but these variations are rather limited. Bastnäsite shows a very limited variation in composition. The search for new REE deposits gives also access to other types of ores than the conventional ones.\textsuperscript{8} Examples include eudialite, euxenite, parisite, synchisite, churchite, gadolinite, fergusonite, loparite and steenstrupine. Phosphate rocks (mainly apatite) used for the production of phosphoric acid and phosphate fertilisers are an important potential REE resource, and was already used in the past for the recovery of REEs.\textsuperscript{9} Even though phosphate rocks contain only small REE concentrations, the excavated volumes are enormous. Rare earths can also be extracted from industrial waste streams such as bauxite residue (red mud), a by-product of the aluminium production and phosphogypsum, a by-product of the phosphoric acid production from phosphate rocks.\textsuperscript{10} Bauxite residue is quite rich in scandium.\textsuperscript{11} By combining the REE concentrates obtained from different REE resources, it is possible to compose a mixed concentrate with a composition that is reflecting much better the needs of the individual REEs by the market than in the case when only one single or just a few types of REE ores are used. By combining the REE concentration from different ores, it is also possible to create a mixed REE feed solution of constant composition. This is beneficial for the optimisation of solvent extraction processes for the separation of mixtures of REEs.

**Solution 2: Recycling**

Recycling and closing the materials loop are very important activities for bringing the REE markets in balance.\textsuperscript{12,13} Recycling of neodymium and dysprosium from end-of-life NdFeB magnets implicates that less primary REE ores have to be excavated to meet the global demand of neodymium and dysprosium. Less mining of REE ores implies less overproduction of cerium and samarium. Recycling of europium, terbium and yttrium from lamp phosphors also helps to keep the HREE market into balance.\textsuperscript{14} Thus, by recycling REEs that are essential for high-volume applications, an oversupply of REEs that are less in demand can be avoided. The REE concentrate obtained by recovery of REEs from end-of-life consumer goods can be used to adjust the composition of the feed of solvent extraction batteries. Recycling is industrially relevant for the most valuable applications: permanent magnets, lamp phosphors and NiMH batteries.
However, several challenging remain to be dissolved, especially the recovery of permanent magnets from shredded waste.\textsuperscript{15,16} To estimate the possible impact of recycling on the REE markets, it is of importance to get an idea of the global inventory of the different REEs in use, of the life cycle of REEs in applications and of the life span of REE-containing devices. Recently, several research groups started to address this issue.\textsuperscript{7,17-22} Recycling of ceria (from polishing powders and car exhaust catalysts) could be recommended from a sustainable point of view, but it will not help to solve the Balance Problem due to the oversupply of cerium on the market.\textsuperscript{23}

**Solution 3: Substitution**

Substitution includes the replacement of one element by another in a given application. The different REEs have very different electronic and magnetic properties so that one REE cannot simply replaced by another REE in an application. For instance, europium is the only REE that can be used in red lamp phosphors. In fact, europium is unique for its line-emission in the red spectral region. In this case, substitution of europium by another REE is not an option. However, in other cases a more critical REE can be replaced by a less critical one or, even better, by a non-critical REE. The NdFeB magnets are a good example of an application where substitution can play a role.\textsuperscript{24} Part of the neodymium (up to 25\%) can be replaced by praseodymium without significantly changing the magnetic properties of the material. This is a very good opportunity to consume a large part of the supply of praseodymium (which is less abundant than neodymium, but has also less specific applications) and to help bringing the LREE market in balance. This also means that there is no need to use very high purity neodymium in NdFeB magnets; didymium (the old name used for the mixture of neodymium and praseodymium) can be used as well. However, it is not possible to replace part of the neodymium in NdFeB magnets by samarium. Part of the dysprosium in NdFeB magnets can be replaced by terbium. This is not often done at present because terbium is a very critical element due to its use in the green lamp phosphors. However, it can be anticipated that more terbium will become available for use in NdFeB magnets if the fluorescent lamps will increasingly be replaced by LEDs (\textit{vide supra}).

What about the replacement of neodymium-iron-boron magnets by samarium-cobalt magnets? As described above, SmCo magnets are in use for a longer time than the NdFeB magnets and for a long time samarium was the most critical REE element in so far that the production of SmCo magnets was limited by shortages in supply of samarium, with very high samarium prices as a result. After 1985, SmCo magnets have been rapidly replaced by NdFeB magnets. NdFeB magnets have a higher energy density than SmCo magnets, but, more importantly, NdFeB magnets are much cheaper than SmCo magnets. More than 70\% of the mass of NdFeB magnets consists of cheap
iron, while the natural abundance of neodymium is much higher than that of samarium. Furthermore, the SmCo magnets contain also the rather expensive cobalt. However, SmCo magnets have some advantages compared to NdFeB magnets: they are much more resistant to demagnetisation at higher temperatures and they are much more corrosion resistant (SmCo magnets do not need to be coated by an anticorrosion layer, in contrast to NdFeB magnets). Therefore, SmCo magnets are used in high temperature applications and in applications where corrosion can be an issue. Typical markets for SmCo magnets are the aircraft industry and the military industry. Still, the market of SmCo magnets is very small compared to the huge market of NdFeB magnets. As indicated above, the share of SmCo magnets in the permanent magnet market is less than 2%. Given the criticality of neodymium/dysprosium and the oversupply of samarium, why cannot more SmCo magnets by produced? First of all, SmCo magnets are more expensive than NdFeB magnets due to the large quantities of cobalt they contain. Cobalt is not a cheap element and it has suffered from also its own supply risks in the past. Cobalt is also used in lithium-ion-batteries, in the form of lithium cobalt oxide (LiCoO₂) in cathode materials. Secondly, the safety regulations for working with samarium in an industrial environment have become more strict. Samarium has two naturally occurring radioisotopes, which are long-lived α-emitters: 147Sm (t½ = 1.06 × 10¹¹ y; natural abundance = 14.99%) and 148Sm (t½ = 7 × 10¹³ y; natural abundance = 11.24%). Working with bulk samples such as in SmCo magnets or with samarium-containing solutions is not a problem, but working with Sm₂O₃ powder (which is a precursor for Sm alloys) is restricted by safety regulations due to the dangers associated with possible inhalation of powders of α-emitters.

Substitution can also mean replacement of REEs by non-REEs, even though this can lead to products with poor, yet still acceptable, performance. Examples include fluid cracking catalysts based on zeolites without REEs. NdFeB or SmCo magnets can be replaced by ferrite or alnico magnets, but these magnets have much lower energy densities. Therefore, REE magnets are unlikely to be replaced in applications where miniaturisation is of importance. Major research efforts are directed to the development of cerium-based magnetic materials. Until 1975, mischmetal was often used for nodularising graphite in cast iron and for desulphurising steel, but these metallurgical applications became largely obsolete due to better production methods and replacement of mischmetal by calcium or magnesium. Ceria in polishing materials could be replaced by alumina or iron oxide, but this is at present not a feasible option since there is an oversupply of cerium. NiMH batteries, containing large quantities of LREEs and especially of lanthanum, could be replaced by lithium-ion batteries. Likewise, the LaNi₅ alloy in NiMH batteries could be replaced by an REE-free titanium-iron alloy. Sometimes, substitution can be more drastic by simply replacing one element by another one, and a totally new technology is introduced on the market, making the older technology based on REEs obsolete. Until about 10 to 15 years ago,
Europium was an important component of red cathodoluminescent phosphors used in cathode-ray tubes (CRTs) for colour television screens and computer monitors. The CRTs screens were replaced by plasma displays (still containing REE phosphors) and LCD screens (using REEs in the phosphors of the backlight fluorescent lamps), but modern OLED screens do not contain REEs at all. A similar evolution is taking place by the replacement of fluorescent lamps by LEDs.

**Solution 4: Reduced use**

By clever engineering, it is possible to reduce the consumption of critical REEs in a given application, without compromising the performance of the REE-containing devices. The NdFeB magnets, which contain dysprosium to protect the magnetic material against demagnetisation at higher temperatures, are a good example. By grain boundary diffusion, the dysprosium is concentrated near the grain boundaries of a sintered NdFeB magnet. As a consequence the required total dysprosium concentration can be decreased by more than 50%.

It is important not to waste critical REEs in applications that do not required purified REEs. In the past, no efforts were made to remove neodymium from the concentrate that was used to prepare mischmetal, although the presence of neodymium was not essential for applications of mischmetal. At present, neodymium is too valuable for magnet applications and is removed prior to mischmetal production.

**Solution 5: New high-volume applications**

Compared to the other REEs, lanthanum and especially cerium are very abundant and cheap. For western REE mining companies, the lanthanum and cerium content of their ores often has a negative effect on the REE basket value and, subsequently, these elements are a nuisance for these companies. Therefore, it is important to develop new high-volume applications for these elements. Research in this area must be encouraged. An example of an emerging high-volume low-tech application is the use of chlorides of lanthanum, cerium or mixtures thereof in water purification technology for removal of dissolved phosphate ions from water. The trivalent REE ions have a high affinity of phosphate ions, resulting in the formation of poorly soluble and readily filterable REE phosphates. Cerium is being investigated as active component in redox flow batteries, for instance the zinc-cerium redox flow battery. Other applications of cerium include its use for the destructive total oxidation of toxic organic compounds and as a redox mediator in organic electrosynthesis.
Thorium

The thorium issue is related to the Balance Problem. Nearly all REE ores contain the radioactive elements thorium and uranium. Although the uranium content of typical REE ores is low, the thorium content of some REE ores can be high. For instance, monazite can contain more than 15 wt% of thorium. Natural thorium is a mono-isotopic element: all but some traces of natural thorium consist of the isotope $^{232}\text{Th}$, an $\alpha$-emitter with a half-life of 14.05 billion years. Due to the safety regulations associated with the handling of naturally occurring radioactive materials, the thorium content of REE ores is a major issue for REE producers. At present, there are no large scale applications of thorium. Furthermore, thorium is considered as radioactive waste and its disposal can be very expensive. The thorium content of monazite is the reason why Rhône-Poulenc (now Solvay) stopped processing monazite at the REE production plant of La Rochelle in France in 1994. The thorium content of the REE ore of Bayan Obo is causing severe environmental issues in Baotou (PR China). As long as thorium is considered as radioactive waste, it will increase the production costs of the rare earths. The costs of thorium waste disposal need to be shared by the different REE applications. However, thorium could be used as a nuclear fuel instead of uranium. Thorium can be used in conventional light-water nuclear reactors, although in that case ThO$_2$ has to be mixed with plutonium oxide. Canadian CANDU reactors can burn thorium as well. A much better approach is to use specially designed nuclear reactors such as the molten salt thorium reactor, which do not need the use of plutonium. Interestingly, the REEs were once by-products of the thorium production. Thorium was used at the end of the 19th century and the first half of the 20th century to prepare incandescent gas mantles ($99\% \text{ThO}_2+1\% \text{CeO}_2$) and the REEs were considered more or less as a waste product, although there were some applications for cerium and mischmetal. Contrastingly, at present thorium is considered as a dangerous waste product. However, the transition to a thorium-based nuclear fuel cycle could lead to zero waste valorisation of thorium-containing REE ores, so that both REEs and thorium can be considered as valuable resources. A positive side effect is that no special thorium mines need to be opened, because it can be expected that the quantity of thorium of processing monazite and other thorium-containing REE minerals is sufficient to cover the global demand of thorium.

Conclusions

The Balance Problem is an intrinsic problem of REE markets that is caused by the imbalance between the demand of individual REEs and their natural abundance in REE ores. Keeping the REE markets in balance is of strategic importance, not only to secure the supply of all REEs required for technological and other applications, but also to avoid dramatic price shocks for critical REEs. Different solutions have been proposed
to solve the Balance Problem: diversification of REE resources, recycling, substitution, reduced use and new high-volume applications. There is no silver bullet solution for this problem. However, by combining different strategies the Balance Problem can be mitigated. The presence of thorium in most of the REE ores is related to Balance Problem: thorium is now considered as an expensive radioactive waste, but this waste could be turned into a resource by using thorium in a thorium-based nuclear fuel cycle. At present there is too much focus on the figures with respect to the total REE ore reserves and/or the total REOs production numbers. It must be realised that most of the current high-tech applications of REEs require the use of purified individual REEs rather than mixtures of REEs. Therefore, it cannot be stressed enough how important it is to effectively deal with the Balance Problem.

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References

Session II: European Rare Earth Resources (Plenary)
UNLOCKING THE POTENTIAL OF RARE EARTH RESOURCES IN EUROPE

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Abstract

During the last decade the non-energy raw materials have become part of the EU’s new industrial strategy and growth agenda, with increased funding opportunities in the field of mineral resources. The four-year (2009–2013) ProMine project has provided a well documented knowledge base of Europe’s non-energy raw material resource potential. The ongoing EURARE project is focused on enhancing the value chain perspectives for European Rare Earth Elements (REE) and the Minerals 4EU project aims to provide harmonized data on European mineral resources. This paper summarises ongoing work by the EURARE project (www.eurare.eu). REE mineral potential belts, including genetic types related to igneous, hydrothermal and sedimentary processes, have been identified across Europe. Potential REE deposits are hosted by carbonatites, alkaline igneous complexes and volcanic successions, granitic pegmatites, iron oxide copper gold deposits, and skarns, as well as secondary deposits such as laterites, bauxites and heavy mineral sands. This paper considers issues of the various deposit types with respect to REE-bearing minerals, grades, volumes, Heavy (HREE) to Light REE (LREE) ratios, radioactive element concentrations, genetic aspects, all in a perspective of raising the awareness for exploration and the potential for exploitation.

Introduction

The European Union (EU) is highly dependent on imports of mineral raw materials that are crucial for a strong European industrial base, sustainable and competitive growth, and a thriving society. A specific group of minerals and metals are characterized as critical raw materials, because they are considered to have significant economic importance for the EU but have clear risks to their supply (1). All the rare earth elements (REE) belong within this group because of their importance in electronics and green technologies, and the dominance of China in their production. For several metals used in electronics and green technology industries, including the REE and platinum group elements, the EU completely relies on imports. The resulting annual shortage is about €11 billion, of which 90% corresponds to metallic minerals, particularly those of major high-tech applications. Recycling of metal scrap represents around 40% to 60% of the input to the EU’s metal production, according to industry estimates.
Rare Earth Elements (REE) is the collective name for 17 chemically similar metallic elements (the lanthanides, scandium and yttrium) that occur together in a wide range of minerals and are mined collectively. They are usually divided into the light REE (LREE) and the heavy REE (HREE); the latter are found in relatively lower concentrations in the Earth’s crust. China today controls about 95% of the world’s REE production, making the supply of these elements for European industry highly vulnerable (2).

At the same time, Europe’s mineral potential is under-explored, both with regard to the subsurface (particularly deeper than 150 metres), and the sea-bed in the EU member states’ exclusive economic zones. Major opportunities for access to raw materials exist within the EU today, especially for mining at greater depths or in small deposits. The sea-bed could also contain valuable raw materials, including REE deposits, leading to growing world-wide competition for marine mineral deposits. More intense and advanced exploration for REE mineral deposits on land and in the marine environment is therefore needed, and seafloor mineral resources are the subject of growing European interest.

This paper aims to provide an overview of different REE mineral deposit types in Europe, and to provide a basis for further research into the mineralizing processes causing REE enrichments, and controlling the formation of feasible grades and volumes. It intends also to deliver some preliminary guides for exploration and exploitation potential.

**Available datasets**

Mineral occurrence databases exist for most countries, but they typically lack full information on REE resources, and very rarely include quantitative estimates of the resource size or how likely it is to go into production. This paper summarises the information that is available from a number of projects carried out under various EU funding schemes and commissioned studies (Fig.1), as follows:

- ProMine ([http://promine.gtk.fi](http://promine.gtk.fi)) has produced a pan-European primary mineral occurrence database and anthropogenic concentration (mainly mining wastes) database, which also contains REE information (3,4). About 270 REE occurrences were recorded. However this database does not provide information on size of occurrence or on ratio of LREE to HREE.

- EuroGeoSource ([http://www.europeosource.eu](http://www.europeosource.eu)) has collected mineral resource information, but only REE occurrences in Greenland are present.

- EuRare ([http://www.eurare.eu](http://www.eurare.eu)) aims to set the basis for the development of a European rare earth element (REE) industry by safeguarding the uninterrupted supply of REE raw materials and products crucial for sectors of the EU economy. It will define and assess all exploitable REE mineral resources and REE demand in Europe (Appendix I), and develop an Integrated Knowledge Management System (IKMS) for EU REE resources, which will provide information on REE and build up the knowledge to be developed within the frame of the project.
• Minerals4EU (http://www.minerals4eu.eu/) will include the development of an EU Minerals Knowledge Base Platform that goes along and in line with the Strategic Implementation Plan for European Innovation Partnership on Raw Materials, and a Minerals Yearbook that will include resource and reserve data for primary minerals. Publication is anticipated in 2015.

• Production statistic data are compiled on a yearly basis by British Geological Survey (BGS) staff (https://www.bgs.ac.uk/mineralsuk/statistics/europeanStatistics.html). The numbers are based on data that are obtained from the national statistical agencies or geological surveys within the individual countries. These data are usually easily obtainable since companies are being taxed according to the actual production, and therefore obligations exist in most countries to report such information to the public authorities.

European geology and metallogeny
The geological evolution of Europe extends over some 3.8 billion years of Earth history. The oldest rocks in Europe are found in the Archaen cratons of Greenland, the UK, and the Scandinavian countries, whilst the youngest Cenozoic rocks are formed along the Mediterranean and Atlantic fringes. The rocks of Europe have been affected by a large number of orogenic events, such as the Svecofennian and Caledonian orogenies in the north and the Variscan and Alpine ones in central and southern Europe. These generated various types and grades of deformation and metamorphism, associated with a range of compositions and volumes of magmatic lithologies emplaced into widely varying tectonomagmatic settings. Metallogenetic evolution throughout this period resulted in emplacement of several major mineral belts, such as the Fennoscandian VMS, IOCG and Iron Oxide deposits, the Iberian Pyrite belt, and the porphyry Cu and epithermal Au Carpathian-Balkan belt (3). Years of research have led to a good understanding of base and precious metal, copper, nickel and iron occurrences, but the genetic processes related to REE mineralisation are not as well understood. The importance of understanding tectonic setting in REE exploration is developed further by Goodenough et al. (this volume).

Primary resources: proposed genetic type classification
The majority of significant primary REE resources in Europe are in alkaline igneous rocks and carbonatites, and the most important deposits occur in extensional rift-related igneous provinces of a range of ages (Goodenough et al., this volume). In Northern Europe, these igneous provinces are deeply eroded and the major deposits lie within plutonic silicate and carbonatite igneous rocks, such as the spectacularly layered peralkaline syenites of the Ilimaussaq intrusion in southwest Greenland (Kringlerne and Kvanefjeld deposits; 5) or the Norra Kārr syenite in Sweden (6). Also of importance across Europe, but most particularly in Sweden, are zones of hydrothermal and pegmatite mineralization. In many cases the source of the REE in these
mineralizing systems is not well understood. Each primary deposit has a different, commonly very complex, ore mineralogy and many REE-bearing minerals also have high contents of U and Th. For this reason, each deposit presents its own challenges in processing, and a range of factors will affect the economic and environmental case for the deposit.

In Southern Europe, the rift-related provinces are at much shallower levels of erosion, and the surface expression of alkaline magmatism is in alkaline volcanic rocks that do not contain significant REE concentrations. In these areas, secondary deposits formed by weathering (bauxites and laterites) and sedimentary processes are more important. It is likely that primary REE deposits remain to be discovered at depth within these rift zones.

Classification systems currently used by BGS, USGS and in Australia, as well as modified versions developed and applied in the ProMine, ASTER (7) and EuroGeoSource projects, have been evaluated, integrated and adjusted to fit the geological setting, metallogenetic evolution and mineral belts in Europe, as part of the EURARE project. Taking into account the INSPIRE Mineral Deposit Group and Mineral Deposit Type code lists, a simplified genetic classification approach (host rock type, mineral forming processes and composition, and LREE and HREE concentration and distribution) is applied, dividing REE mineralisations/deposits into two main categories:

- **Primary deposits** (Fig.1) linked to magmatic and hydrothermal REE-mineral forming processes:
  - Carbonatites (LREE-enriched deposits with bastnäsite, allanite, apatite and monazite as the main minerals e.g. Fen in Norway, Sökli in Finland (8), Sarfartoq and Qaqqarssuk (9) in west Greenland)
  - Alkaline-peralkaline igneous rocks (LREE- or HREE-enriched deposits with apatite, eudialyte, gadolinite and loparite among the main minerals e.g. Norra Kärr in Sweden (6), Katjakangas in Finland, Kvanefjeld and Kringlerne in south Greenland). This deposit type includes the largest resources known in Europe at present.
  - Iron Oxide Apatite (IOA) and Iron Oxide Copper Gold (IOC) deposits (usually LREE-enriched with apatite and/or allanite e.g. Kiruna magnetite-apatite deposits (10) in Sweden)
  - Granitic pegmatites (ranging from LREE-enriched, containing allanite and monazite, to HREE-enriched with gadolinite as main mineral e.g. Ytterby mineralisation in Sweden, Evje-Iveland pegmatite district in Norway)
  - Hydrothermal/hydrogenetic (mainly LREE-enriched and varying grades, with bastnäsite, allanite, monazite, gadolinite and parasite as common minerals e.g. Bastnäs-Norberg-Nora (11) skarn mineralisation zone in Sweden)
  - Sedimentary concentrations on land and in the marine (12) environment (e.g. LREE-enriched in U-deposits, fluorite-barite mineralisations, with disseminations of synchysite and parasite, phosphates in NW Greece on land, and REE mineralisations associated with deep sea-floor polymetallic nodules and cobalt-rich crusts)

- **Secondary deposits** (Fig.1) related mainly to sedimentary remobilization and weathering processes of mainly REE-bearing igneous rocks:
  - Placers, of paleo-, marine and alluvial affiliation (commonly LREE and U-Th enriched, with monazite, xenotime, allanite as common minerals, e.g. Nea Peramos coastal heavy sands in northern Greece, Klocktorpet and Tåsjö pale placer apatite mineralisations in Sweden)
  - Residual-lateritic/bauxitic (usually LREE-enriched, high-graded and monazitic e.g. central Greece monazite-bastnäsite lateritic/bauxitic mineralisations),
Ion-adsorption clays/residual clays (HREE-enriched, commonly low-grade high-volume, associated with weathered REE-bearing granites, with REE being adsorbed by clay minerals such as kaolin and halloysite).

Secondary resources
Secondary resources are those not directly derived from natural REE occurrences, but rather from material that has already been used by humans. Mining wastes, including various waste streams such as weakly mineralized waste rocks, processing tailings and metallurgical residues, could turn out to be potential resources for recovery of exploitable grades of REE. The abandoned historical mine waste dumps in Bastnäs district and the stockpiled apatite leftovers in Kiruna, both in Sweden, as well as the red mud residues of Al smelting in Greece and elsewhere in Europe (Deady et al., this volume), are prominent examples of raw materials that might be secondary resources of REE. Recycling of material from the consumer electronics industries represents another source of the REE (2). However, in spite of the fact that recycling is a vital component of a resource efficient economy and a long-term target to secure REE supply, the EU will still be very much dependent on primary mineral resources extraction for the foreseeable future.

Exploration data availability
There have been several national-based geochemical surveys that have carried out soil, bedrock and stream sediment sampling across Europe. Many EU member states have produced geochemical maps for varying subsets of the REE on national and regional scales. However this information, although very valuable in regional-scale REE exploration campaigns, is rather variable and fragmented, and requires much harmonization before Europe-wide REE mineralised belts can be recognised. Projects reporting data and delivering pan-European geochemical maps include FOREGS (13,) and GEMAS (http://www.eurogeosurveys.org/projects/gemas/), carried out by the EuroGeoSurveys Geochemistry Expert Group, the latter based on sampling of agricultural and grazing land soils (14, 15, and 16).

Geophysical measurements applying airborne and ground magnetic, electromagnetic and gravimetric methods have been conducted across Europe on national and regional scales. They may provide valuable data and offer efficient REE exploration tools at a range of scales, but this is based more on the interpretation of the responses and signatures received from the wall and host rocks of the mineralisation rather than the REE mineralisation itself. As yet there is limited information to show how interpretation of geophysical data may be better used to pinpoint REE mineralization.
Fig. 1: Overview of major REE mineralisation types in Europe and Greenland based on EURARE data and information (17). There is obvious exploration potential and high prospective interest for primary deposits in Greenland, the Nordic countries and the British islands, and secondary deposits in mainly NW France, Greece and west Balkans.

**Preliminary recommendations**

**Economic aspects**

There are some advanced REE projects listed on Table I, providing an overview of developments taking place in Europe. Economically feasible projects in Europe are progressing in Sweden (Norra Kärr) and Greenland (Kringlerne and Kvanefjeld) with a total potential (resources and reserves) of all three together in the order of 30 million tonnes REO. The trend in Europe is the same as in the rest of the world since 1960s, showing that REE mining projects are mainly related to primary deposit types associated with carbonatites and alkaline igneous rocks, compared to prior to 1950 when most bulk REE production was derived from monazite-bearing placers.
Table I: Major REE advanced projects in Europe and Greenland

<table>
<thead>
<tr>
<th>Deposit name</th>
<th>Country</th>
<th>Type</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norra Kärr</td>
<td>Sweden</td>
<td>Alkaline igneous</td>
<td>41.6 Mt @ 0.57% TREO</td>
</tr>
<tr>
<td>Olserum</td>
<td>Sweden</td>
<td>Iron oxide - apatite</td>
<td>4.5 Mt @ 0.6% TREO</td>
</tr>
<tr>
<td>Kvanefjeld</td>
<td>Greenland</td>
<td>Alkaline igneous</td>
<td>122 Mt @ 1.4% TREO</td>
</tr>
<tr>
<td>Sarfartoq</td>
<td>Greenland</td>
<td>Carbonatite</td>
<td>5.9 Mt @ 1.8% TREO</td>
</tr>
<tr>
<td>Aksu Diamas</td>
<td>Turkey</td>
<td>Placer</td>
<td>494 Mt @ 0.07% TREO</td>
</tr>
</tbody>
</table>

Exploitation potential

Based on the geological and compositional characteristics of the major REE mineralisation types in Europe and Greenland, it is obvious that the strongest exploration potential and highest prospective interest are for primary deposits in Greenland and the Nordic countries, and secondary deposits in NW France, Greece and the west Balkans. A range of factors may affect exploitation potential of REE deposits: these include ratio of more valuable HREE to LREE; overall grade and tonnage; content of the radioactive elements; environmental considerations; proximity to transport and infrastructure; and availability of processing routes for the deposit type and mineralogy. Currently, the larger, high-grade carbonatites and alkaline rocks are of highest exploration potential and priority, but processing of these hard-rock deposits is energy intensive and costly. For this reason, development of new exploitation technologies could mean that the lower-grade but more easily processed secondary deposits may grow in importance.

More efficient exploration

Mineral exploration is the only way to ensure secure and sustainable supply of raw materials. Even if 100% recycling efficiency is attained this will never be able to meet the increasing supply demand for REE. Exploration has for many years been focused on base metal sulphide and iron oxide mineralised environments. New advanced technologies related to geochemistry and geophysics were mainly developed to fit to the geological and metallogenetic characteristics of these systems. There is now a need to better understand the REE ore forming processes of all the primary and secondary deposit types, in order to develop the right exploration guides and apply them to European geological settings, making the discovery of new ore deposits possible. Carbonatites and alkaline rocks may be of high priority but other types such
as the granitic pegmatite IOA & IOCG ones need to be explored more efficiently. Examples of required end products might be,

- Distribution of REE (total, HREE, LREE and individual elements) occurrences in Europe (Map)
- Reserves and resources in Europe and in individual countries (Reports, Excel spreadsheets, maps)
- Mineral potential maps for the REE in Europe

Acknowledgements

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THE WORLD-CLASS REE DEPOSIT TANBREEZ, SOUTH GREENLAND: ITS SIZE AND STRUCTURE

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Abstract

The Tanbreez ore deposit is a highly fractionated ortho-magmatic Zr-Nb-Ta-REE deposit in the southern part of the 1.13Ga old Ilímaussaq intrusive complex in South Greenland. The commodities are hosted in the zirconosilicate mineral eudialyte, occurring concentrated in kakortokite at the floor of the exposed intrusion. The kakortokite sequence is outcropping over an area of 5 x 2.5 km and has a total thickness of 335 m. A conservative estimate specifies the resource to more than 4 billion tons. Linear correlations between ZrO₂ and individual REE indicate that eudialyte is by far the main REE bearing mineral in kakortokite. Estimated average grades are 1.75% ZrO₂, 0.18% Nb₂O₅ and 0.6% total REO, of which heavy REE make up 30% (including yttrium).

Introduction

Many of the metals used in today’s technology such as REE are enriched in alkaline and carbonatitic intrusive complexes. The rare earth market is dominated by China. Therefore there is a concern outside China about supply of these elements. This has launched an exploration activity for these elements all over the world. Greenland, which is known for its alkaline igneous provinces, has been the focus for the industries REE exploration for the last 10-15 years.

The Ilímaussaq alkaline complex in southern Greenland host several mineral deposits one of which is Tanbreez, a world class REE deposit. The anagram, Tanbreez, is based on the major elements (Ta-Nb-REE-Zr) contained in the deposit. Moreover, there are elevated concentrations of the elements Hf and Y. Uniquely; all the commodities are contained in the mineral eudialyte, which is a rock-forming mineral in the apaitic nepheline syenite kakortokite.

Rimbal Pty Ltd, the Australian owner of Tanbreez Mining Greenland A/S, holds an exploration license since 2001 over the deposit and has invested the last 13 years in understanding and testing the deposit. The previously existing knowledge, dating as far back as 1880’s, included drilling and mapping programs and extensive metallurgical test programs carried out by former license holder has contributed to the present knowledge of the deposit.
In this contribution we describe the structure and thickness of the kakortokite (ore host sequence) and its contact relationships to the rocks surrounding it. Furthermore, we show the geochemical correlation of REE and Zr in kakortokite, including an estimate on the overall size of the deposit.

**Geological Setting**

The Meso-Proterozoic Gardar Province in South Greenland contains 10 intrusive complexes that range in composition from alkali granite to nepheline syenites and gabbroic dikes. These rocks intruded the 1.9 Ga old Julianenhåb granite basement that is unconformably overlain by sandstones and basalts of the Eriksfjord formation. The alkaline to agpaitic Ilímaussaq intrusion has been dated at 1.13 ± 0.05Ga (Sm-Nd mineral isochron) and belongs to the younger Gardar event. The intrusion is 17 km x 8 km in size and at least 3 km thick. The composite intrusion is cut by the Tunulliarfik Fjord (Fig 1). The geology of the Ilímaussaq intrusive complex has been described as a succession of three main phases that crystallized at about 3-4 km depth.

**Fig. 1A)** Geological map of the Ilímaussaq intrusion. **B)** Satellite image of the southern part of the intrusion with the exploration license area in green. Also shown is the drill hole location of the stratigraphic hole in the central part of the kakortokite.
Phase 1 is an outer ring dyke of augite syenite, which partly rims the complex to the west, east and south and is up to 1 km wide. The augite syenite also overlies the intrusive complex.
Phase 2 is alkali granite and quartz syenite in the roof zone of the complex.
Phase 3 consists of peralkaline rocks, evolving into the dominant agpaitic nepheline syenite of the complex. This phase can be subdivided into a:
Roof sequence that crystallizes from the roof downwards, forming the following succession of rocks downwards: pulaskite, foyaite, sodalite foyaite and naujaite (Fig. 1 naujaite-foyaite series). The three first mentioned rock types occur as a thin, but persistent cover of part of the complex on both sides of the Tunulliarfik Fjord (Fig 1a). The naujaite is by far the thickest unit of the roof sequence with a thickness between 600 m and 800 m.
Floor sequence solidifying upwards. The floor sequence consists of a rhythmically layered rock called kakortokite.
Intermediate series that is sandwiched between roof and floor series, consisting of different types of lujavrites.
The kakortokite contains a significant amount of the mineral eudialyte, and hence, is enriched in zirconium, rare earth elements, niobium and tantalum. The kakortokite sequence is regarded as the host of a world-class, multi-element deposit.

**The structure of the kakortokite body**

Kakortokite and lujavrite constitute the lower sequence of the stratified intrusion where kakortokite is overlain by lujavrite. The exposed thickness of the two rock types is nearly 1000 m.  
The kakortokite has been subdivided into three parts. From bottom to top:
- Lower layered kakortokite (LLK)  (approx 209 m thick)
- Slightly layered kakortokite (SLK)  (approx 35 m thick)
- Transitional layered kakortokite (TLK)  (approx 40 m thick).

All planar elements are locally parallel and the combined structure recalls a simple saucer shaped pattern with steep to vertical structures at the periphery, which rapidly turns into a general dip of 10-15 degrees for the main part of the kakortokite. Steeper dips of the sequence occur just north of Lakseelv, but this is probably linked to drag associated with the Lakseelv Fault (Fig 1b).

The kakortokite sequence is exposed over an area of 5 x 2.5 km on the south side of the Kangerdluarsuk Fjord (Fig 1) and ranges from sea level up to about 400 m asl. The exposed area comprises 95% kakortokite and 5% related rocks, mostly syenite dykes and sills.

The Lower layered kakortokite and the Transitional Layered Kakortokite show subhorizontal layered structures, whereas the Slightly Layered Kakortokite sequence is a virtually unlayered grey and fine-grained kakortokite.
The spectacular layering in LLK is composed of black, red and white layers, depending on the amount of specific minerals. The black layers are rich in the mineral arfvedsonite and contain lesser amounts of eudialyte, alkali-feldspar and nepheline. The red layers are composed of eudialyte, with lesser amounts of arfvedsonite, alkali-feldspar and nepheline, whereas the white layers are composed of alkali-feldspar and nepheline with lesser amounts of arfvedsonite and eudialyte. Locally sodalite occurs as a significant mineral phase.

Conventionally, the three colored layers together form a unit. The exposed part of the kakortokite consists of 29 units labelled +1 to +17 and -1 to -11 above and below unit 0, respectively. The layering can be recognized from a distance; however, in some cases the exact contacts between layers is not always clearly defined close up and in drill core due to more transitional contacts between the main mineral phases of the layers. There is some variation in thickness between the layers as well as in texture and grain size, which helps to identify some horizons. On average, a unit is about 10-13 m thick. There are, however, units that are not fully developed; in some cases black/red layers are very faint or missing. An average relative thickness of the individual layers is 1.5m for black, 1m for red and 10m for white layers. In general, the eudialyte content (main host for Zr, and REE) of the black and white layers is slightly below 10vol%, whereas the eudialyte content of the red layers is around 30-40 vol%.

Following is a description of the contact relationships of the kakortokite sequence to the upper, lower, and marginal boundaries of the intrusion.

**Boundaries of the kakortokite body**

The upper boundary of the kakortokite sequence is a gradual and concordant boundary to the overlying lujavrite sequence.

The lower boundary of the kakortokite is not exposed, which has led to speculations on the thickness of the kakortokite. Exploration drillings by Tanbreeze Mining Greenland A/S in 2007 in the coastal area of Kangerdluarsuk near the southern boundary of the ilimaussaq intrusion (Fig 1b) encountered a black to grey, porphyritic, fine grained rock with peppered sodalite in the matrix below the kakortokite. The rock contains 5-10 vol% subhedral to euhedral, poikilitic biotite grains 1-2 mm in diameter, and aggregates of aenigmatite, biotite and arfvedsonite in a groundmass of feldspar, nepheline and sodalite. Geochemically the rock composition is equivalent to a tephriphonolite. During drill core logging this rock was temporarily call “Black Madonna” and that name will also be used throughout this paper. Black Madonna was found in 8 drill holes so far, but none of the drill holes has completely penetrated Black Madonna. The longest interval drilled in Black Madonna is 220 meter.

There is a reasonable good correlation of the contact between kakortokite and the massive occurrence of Black Madonna between the drill holes. It is apparent, that the top of Black Madonna is dipping towards the northwest. Based on the limited data it
seems that Black Madonna has a dip similar to the layering of the kakortokite. This was corroborated by the depth of the occurrence of Black Madonna in the stratigraphic hole (DX-01) drilled in 2010 about 1.5 km east of the drillings in 2007 (Fig 1b). This further indicates that Black Madonna could lie under the entire kakortokite sequence. The contact between Black Madonna and the Lower layered kakortokite is well defined without been sharp. In the contact zone rounded inclusions of Black Madonna often 5-10 cm long occur in the layered kakortokite and it is uncorrect to encounter inclusions 50 m or more from the contact. However there is a clear decrease in number of inclusions away from the contact.

A rim of massive agpaitic nepheline syenite, which consists of the same minerals as the layered kakortokite sequence, characterizes the marginal borders of the kakortokite sequence. This led ref. 11 to describe the rocks along the rim as a not banded kakortokite. The rim has also been referred to as marginal pegmatite by ref. 9, 12. Because the rim is a complex mixture of different eudialyte-bearing rock types, including pegmatite, a more appropriate name would be ‘border zone’ of the kakortokite. The border zone represents a transition between the layered kakortokite and the augite syenite ring dyke of the Ilímaussaq intrusion (Fig 1a). The border zone is about 150 m wide at sea level at Kangerluarsuk and decrease to about 50 m at an altitude of about 450 m. The zone is made up of eudialyte-bearing nepheline syenite, which shows a variation in texture from medium to coarse-grained massive rock The inner boundary of the border zone against the kakortokite is gradual over about 5-10 m where the layering becomes more subtle and turns into a massive agpaitic rock. The outer boundary of the border zone towards the augite syenite is subvertical, sharp and without a chilled margin. The border zone’s complex intergrowth of texturally different kakortokite like rocks is cut by a eudialyte poor pegmatite mainly containing feldspar, nepheline, sodalite, arfvedsonite and aegirine. The proportion of the pegmatite increases towards the augite syenite and at the same time it largely parallels the augite syenite. In the outer 10 m of the border zone they occur as a subvertical swarm of pegmatite locally associated with hydrothermal alteration. The pegmatite is the youngest member of the border zone and from an economical point of view, down grades part of the border zone and this part will most likely not be subject to mining.

**Size of the kakortokite body**

The exceptionally well-exposed kakortokite in combination with the subhorizontal structure of the sequence were used by ref. 9 to estimate the tonnage of the lower layered kakortokite. The calculation was based on detailed mapping of the 29 rhythmic units in the exposed part of kakortokite. Ref. 13 repeated the estimate based on the geological map: Southern part of the Ilímaussaq Complex, South Greenland, 1:20000 published by Grønlands Geologiske Undersøgelse (1988). Ref. 9 and 13 measured 209m and 218 m, respectively for the total thickness of the lower layered kakortokite,
which is within the expected uncertainty of this kind of survey. The volume of kakortokite was determined using a planimeter to measure the area on the map between the contours of the different rhythmic units.

Exploration drillings in 2007 showed that the lower contact of the kakortokite and Black Madonna occurs about 20 m below sea level on the coast of Kangerluarsuk (Fig 1), which means that 20 m should be added to the thickness measured on the surface. Assuming 214 m as the average for the layered kakortokite based on the previous studies, the total thickness becomes 234 m.

Subsequently, the stratigraphic borehole DX-01 (Fig 1b) was drilled in the central part of the kakortokite body in 2010, and shows a total thickness of the lower layered kakortokite of 269 m, which is 35 m more than the measured thickness on the surface.

The difference in thickness cannot convincingly be explained by the uncertainty in the measurements, but is most probably related to structural conditions. This makes the correlation between numbered layers on the surface and the layering observed in drill cores difficult, except for correlation over short distances and involving kakortokite layers with very characteristic textures.

Previous estimates of the tonnage of the lower layered kakortokite west of Laksetværelv (Fig 1b) yielded 3.7 billion tons. The estimate was based on the thickness of the lower layered kakortokite of 209 m, which is 60 m less than the thickness found in drill hole DX-01. The new estimate, using the thickness from DX-01, and using a linear interpolation from previous estimates would increase the tonnage to 4.7 billion tons. This number would increase even more if kakortokite of the slightly layered kakortokite, the transitional layered kakortokite and the border zone would be included.

**Ore Grade**

Resource assessments in earlier studies show a variation in ore grade of the lower layered kakortokite between 1.4% ZrO$_2$ to 1.9% ZrO$_2$. The average ore grades based on assay data from drillings from the area along Kangerluarsuk where the initial mining is planned is 1.75% ZrO$_2$, 0.18% Nb$_2$O$_5$ and 0.6% total REO including yttrium. The commodities are all contained in eudialyte, a Na-rich zirconosilicate mineral. Eudialyte is by far the most abundant Zr-bearing mineral in kakortokite, occurring in the black, white and red layers. The bulk rock data show close linearly correlation between ZrO$_2$ and Nb, Ta and light and heavy REO (Fig 2), which is a clear indication that eudialyte is the dominant REE-bearing mineral.

The distribution of the total REO in the ore (kakortokite) shows a quantity of 30.9% heavy REE (including Y) and 69.1% light REE (Fig 3). Investigations have shown that no or very little cryptic variation occurs in the minerals of kakortokite, consequently, little change in the eudialyte composition is expected in ore and therefore the magnetic properties of eudialyte would remain the same for the benefit of the planned magnetic concentration of eudialyte. Importantly, drill core assays show elements like
U and Th have background values (20ppm and 53ppm, respectively), which is an advantage in processing the ore.

Fig. 2. Assay data showing good correlation between Zr and Dy as a representative of the REE.

Fig. 3. Proportion of the different REE+Y found in the Tanbreez deposit

**Conclusion**

The Tanbreez polymetallic Zr-Nb-Ta-REE deposit is hosted in the Ilímaussaq intrusion in South Greenland. The ore body is made up of kakortokite that is characterized by rhythmically layered units of layers that are either dominated by feldspar, arvedsonite and eudialyte, respectively. The kakortokite sequence is defined by gradual contacts to the overlying lujavrites and an unexposed (only encountered in drill cores) contact zone with numerous xenoliths to the underlying Black Madonna unit. The border zone
contact to the augite syenite ring dike is well defined and the outer part of the zone cut by pegmatoid dikes.

Zr shows perfect correlations with REE in bulk rock analyses, which indicates that the main ore mineral is eudialyte. The thickness of the lower layered kakortokite sequence is a about 270m, and the volume of the ore body equals about 4.7 billion tons of ore. The average ore grade where the initial mining is planned is 1.75% ZrO₂, 0.18% Nb₂O₅ and 0.6% total REO. The proportion of HREE is up to about 30%.

References


Session III-A: European REE Supply and Demand
PRIMARY AND SECONDARY SOURCES OF RARE EARTHS IN THE EU-28: RESULTS OF THEASTER PROJECT

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Abstract

The ASTER project aims at establishing flows and stocks of certain critical rare earth elements at the scale of the EU-28, considering both primary and secondary sources. Material flow analyses were performed taking into account processes along the value chain (separation, manufacture, use, waste management) and including also lithospheric (geologic) stocks. While this paper focuses on fluorescent lamp phosphors (Tb, Eu, Y), a paper by Planchon et al. (this conference) addresses permanent magnets and batteries (Nd, Pr, Dy). Results suggest that given the magnitude of flows in the EU-28, the development of a mining project in Sweden and/or Greenland would contribute significantly to reducing heavy rare earth; e.g. Tb, criticality.

Introduction

Member state and European policies with respect to the safe supply of mineral raw materials aim at improving eco-efficiency1. The objective of eco-efficiency is to increase the quantity of services per unit mass of raw material, while decreasing environmental impacts. One of the pillars of eco-efficiency is recycling. In order to efficiently position the development of innovative recycling processes, it is important to have a clear picture of flows of stocks of mineral raw materials all along the value chain. The on-going ASTER project, started in 2012 for a period of three years, aims at applying material flow analysis (MFA) to selected rare earth elements (REEs) for the EU-28. Certain rare earth elements are deemed “critical”, as they combine importance for strategic sectors of the economy with risks of supply shortage3, 4. The recent JRC report2 identifies six critical REEs (Dy, Eu, Tb, Y, Pr and Nd) that are precisely the REEs that were selected for the ASTER project.

Given the importance of recycling, the ASTER project combines an “application” approach with an “element” approach. Table 1 shows the correspondence between
the two. These three applications were selected because of their importance in terms of use of the selected REEs, and also because recycling processes for these applications either already exist or else are currently under development.

Table 1: Correspondence between applications and REEs addressed in the ASTER project

<table>
<thead>
<tr>
<th>Application</th>
<th>REEs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphor powders</td>
<td>Eu, Tb, U</td>
</tr>
<tr>
<td>Permanent magnets</td>
<td>Nd, Pr, Dy</td>
</tr>
<tr>
<td>NiMH batteries</td>
<td>Nd</td>
</tr>
</tbody>
</table>

While REEs such as Nd are used in a variety of other applications, it was considered of lesser importance to examine, e.g., flows of Nd in ceramics, as there are currently no realistic prospects of recycling Nd contained in these products. In this paper, we adopt the following distinction between light (LREE) and heavy (HREE) rare earth elements:
- LREE : La, Ce, Pr, Nd, Sm;
- HREE : Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu (plus Y).

Methods

A systemic approach

For the case of fluorescent light phosphors, the system that was analysed is described schematically in Figure 1. The figure illustrates a certain number of processes with, starting upstream in the value-chain: separation (S) of rare earth concentrates, fabrication (F) of trichromatic phosphor powders, manufacture (M) of fluorescent lamps (LFL and CFL; resp., linear and compact fluorescent lamps), use (U) of these lamps in the economy, waste management (WM) of end-of-life products and final elimination (landfill and/or dissipation in the environment). These various processes are linked by arrows that represent flows from one to another. Differences between flows into or out of a process imply an addition or subtraction to stock within the process. The dashed line in Figure 1 represents the limits of the studied system (the EU-28). However, an additional “process” appears in Figure 1 indicated as “L” (lithosphere). The lithosphere represents geological potentialities in the form of potential REE resources (as opposed to reserves). For geological and economic reasons, the limits of this process were taken as continental Europe (including the Scandinavian shield and the Kola Peninsula) plus Greenland. Therefore this process straddles the limits of the EU-28.
It is important to note that the system analysed in this study is an “open” system: there are inflows and outflows to and from the system all along the value chain. This is in contrast with most previous REE MFA studies which have addressed global flows and hence a “closed” system. In the latter case, flows can be “constrained” by world mining production, as reported by, e.g., the USGS.

**Figure 1:** Schematic of the system investigated in the case of fluorescent-lamp trichromatic phosphors. LFL = linear fluorescent lamps; CFL = compact fluorescent lamps

Flows were estimated over a number of years exceeding the expected average lifetime of the considered products (taken as 6 years for fluorescent lamps), in order to obtain estimates of in-use stocks. Year 2010 was selected as the reference year for the final results of the calculations, due to data availability at the start of the project.

**Information sources**

Data mining constitutes the main task of any MFA. Sources of information included statistical custom data (EUROSTAT, Global Trade Atlas, etc.), specialized reports, USGS data, company reports on product sales, etc. With respect to the upstream portion of the value chain, the same HS codes (listed in Table 2) were used as in the Öko-Institut report. GTA data for Chinese exports based on 8-digit HS codes that are specific to individual REEs were also used.

These HS codes represent raw products that contain mixtures of REEs. In order to obtain data on individual REEs, a disaggregation method was applied. The method
considers the relative market shares of products containing REEs (e.g., auto catalysts, magnets, batteries, polishing powders, etc.) and the composition of the REE mixtures in each product.

**Table 2: HS codes used for REE-containing products in the upstream portion of the studied system**

<table>
<thead>
<tr>
<th>HS code</th>
<th>Description in EUROSTAT</th>
</tr>
</thead>
<tbody>
<tr>
<td>28053010</td>
<td>Intermixtures or interalloys of rare-earth metals, Scandium and Yttrium</td>
</tr>
<tr>
<td>28053090</td>
<td>Rare-earth metals, Scandium and Yttrium (Excl. intermixtures or interalloys)</td>
</tr>
<tr>
<td>28461000</td>
<td>Cerium compounds</td>
</tr>
<tr>
<td>28469000</td>
<td>Compounds, inorganic or organic, of rare-earth metals, of Yttrium or of Scandium or of mixtures of these metals (Excl. Cerium)</td>
</tr>
</tbody>
</table>

Certain data from EUROSTAT had to be corrected to account for the fact that Austria no longer reports its REE-related data after 2008. GTA data for Austria were disaggregated into imports and exports from intra- and extra EU-28, considering averages calculated over the pre-2008 period.

For the evaluation of geological potentialities in the lithosphere, over 350 occurrences and/or deposits located within the EU-28 were analysed\(^\text{14}\) (see also Charles et al., this conference). The mineralogical characteristics of these deposits and occurrences provide information regarding potential resources, the reliability of which depends largely on the state of progress of exploration projects. However, the objective was to provide orders of magnitude for potential resources (lithospheric stocks), that could be compared with the magnitude of flows in the EU economy.

**Uncertainties and reconciliation**

Information collected in the course of a MFA for critical metals is inevitably fraught with uncertainty. This uncertainty is typically of an “epistemic” (reflecting incomplete knowledge) rather than a “stochastic” (reflecting random variability) nature. Uncertainty implies that MFAs do not balance and therefore reconciliation methods are used\(^\text{15}\). Such methods generally assume that uncertainty can be represented in the form of Gaussian probability distributions (see, e.g., the STAN software\(^\text{9}\)).

However, epistemic uncertainty (such as typically ensues from expert-opinion) is more faithfully represented by the nested intervals (or fuzzy sets) of possibility theory\(^\text{16}\). Therefore, as part of the ASTER project, a methodology was developed for reconciling MFAs under fuzzy constraints\(^\text{17, 18}\). The methodology described in\(^\text{17, 18}\) provides an alternative to the classical least-squares minimization approach, which relies on a purely probabilistic representation of uncertainty, whereas uncertainties in this
context are typically epistemic (reflecting the incomplete/imprecise nature of available information). With the fuzzy-constraint reconciliation methodology, uncertainty relative to flows and/or stocks is represented using fuzzy sets (e.g. a minimum value, a maximum value and a preferred value). The approach then consists in finding the maximum level of consistency between input information, while taking into account the various constraints (mass balances and memberships).

**Results**

The results presented herein are preliminary as the project is still on-going. An important deliverable of the project will be Sankey diagrams for the considered REEs. These diagrams are described qualitatively below for the case of REEs in fluorescent light phosphors.

A first step of the disaggregation procedure consisted in converting tons of products corresponding to the customs data for the HS codes of Table 2, into tons of rare earth oxide mixtures (REOs). The conversion factors were selected based on data from USGS\textsuperscript{12}. For the metals and alloys (codes 280530), the conversion factor is 1.2 based on stoichiometric considerations. For codes 284610 and 284690, conversion factors were taken as, resp., 0.67 and 0.72.

Application of these conversion factors to historical imports and exports of raw products containing REEs in the EU-28 yields Figure 2. The significant decrease in imports observed in 2009 is interpreted as a consequence of the 2008 financial crisis.

![Figure 1: EU-28 imports and exports of REOs based on EUROSTAT (and GTA for Austria post-2008 correction)](image-url)
Application of the disaggregation methodology to these data provides information relative to flows F1 and F2 of Figure 1, which can then be compared with information provided by SOLVAY, the only company in the EU-28 to perform separation of REEs for trichromatic phosphors. Separation is also performed in Estonia by SILMET, but not for phosphor applications (mainly for Nd). Further to separation, SOLVAY produces phosphor precursors that are sent to process “F” (Figure 1) to produce phosphors. Information relative to imports and exports of phosphors is obtained based on HS code 320650 (inorganic products of a kind used as luminophores, whether or not chemically defined). Expert information was necessary to define the typical composition of these phosphors, taking into account that the composition is different for imported versus exported phosphors (in and out of the EU).

Further down the value chain, data was collected for manufactured products containing trichromatic phosphors. The two HS codes of Table 3 were used.

**Table 3: HS codes for fluorescent lamps**

<table>
<thead>
<tr>
<th>HS code</th>
<th>Description in EUROSTAT</th>
</tr>
</thead>
<tbody>
<tr>
<td>31501530</td>
<td>Fluorescent hot cathode discharge lamps (excluding ultraviolet lamps, with double ended cap)</td>
</tr>
<tr>
<td>31501510</td>
<td>Fluorescent hot cathode discharge lamps, with double ended cap (excluding ultraviolet lamps)</td>
</tr>
</tbody>
</table>

Results of the analysis suggest that the orders of magnitude of Tb, Eu and Y flows in the EU-28 related to fluorescent lamp phosphors are resp., 10, 15 and 180 tons. Taking into account the history of flows into use in the EU-28 over a period exceeding the expected average lifetime of the fluorescent lamps, in-use stocks for Tb, Eu and Y in 2010 are estimated as, resp., 140, 220 and 2300 tons. The annual additions to in-use stock in 2010 are estimated to be resp., +8, +13 and +140 tons/yr for these elements.

With respect to flows F13 and F14 in Figure 1 (recycling), there was no recycling in 2010 in the EU-28, as SOLVAY started its recycling operations (in Saint-Fons and La Rochelle, France) in 2012. As an indication, the order of magnitude of Tb recycled each year is a few tons per year.

These figures can be compared to geological potentialities derived based on the analysis of three important REE projects: the Norra Kärr project in Sweden and two exploration projects in Greenland (Kvanefjeld and Kringlerne). The Norra Kärr project is well advanced and has recently received the authorization to operate from the Swedish government. We estimate the resource of Tb at this site to be on the order of 2 000 tons. The potentials of Kvanefjeld and especially Kringlerne are far superior (resp. 10 000 and 110 000 tons Tb), however, the likelihood of these projects entering into production is much lower, due in particular to environmental constraints and
social acceptability. Nevertheless, these figures suggest that if just one of these projects enters the production phase (with Norra Kärr as the most likely candidate), the criticality with respect to certain heavy REEs such as Tb will be significantly reduced.

**Conclusions**

Results of the on-going ASTER project provide estimates of flows and stocks of certain REEs considered as critical. This paper addresses the results relative to REEs in fluorescent lamp phosphors, while another paper (Planchon et al., this conference) addresses Nd and Dy.

The data collected to-date suggest a somewhat “reassuring” picture with respect to criticality of Tb, Eu and Y. It is the opinion of the authors of this paper that the crisis regarding REEs that was experienced in 2011 is essentially over. It is reminded that in July 2011, peak prices of Dy and Tb exceeded average prices over the period 2002-2009 by factors on the order of, resp., 20 and 10, as a result of stricter quotas on Chinese exports. Several factors have contributed to reducing the pressure on these substances. On the one hand, countries that import REEs have diversified their sources of supply of LREEs (e.g., Mount Weld in Australia and Mountain Pass in the U.S.). Also, there are currently considerable efforts devoted to optimizing the quantities of REEs used in products, as for example Dy in permanent magnets. Substitution is also an important issue. Regarding Tb, the development of LED lighting, which use very little REEs and virtually no Tb, will contribute in the future to reducing the pressure on this element. In the case of Eu in fact, the development of LEDs could very well lead to a large excess of supply versus requirements in the relatively near-future.

Detailed results of the ASTER project are currently in the process of being published. It is anticipated that the approach of associating both primary and secondary sources in the systemic analysis of critical metals will be applied to other substances (e.g., In, Ge, Ga, etc.), as is the case for projects that have already been initiated. It should be noted however that, as for REEs, data regarding such “small” metals are hard to come by. On the one hand, there is very little information available regarding reliable estimates of resources for substances that are essentially by-products of carrier metals. Also, considerable effort is still needed to quantify the quantities of these substances in products, where they may be present in very low concentrations (on the order of a ppm). Such information is crucial in order to evaluate the economic feasibility of recycling processes.
Acknowledgments

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15. COM. Roadmap to a resource efficient Europe. COM 571, European Commission, Brussels, 2011.
THE ROLE OF RARE EARTHS SUPPLY RISK IN LOW CARBON TECHNOLOGIES INNOVATION

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Abstract

Considering the quest for alternative energy and transportation modes and their importance for sustainable growth, this paper examines to what extent the supply risk of rare earths poses a barrier to the increased adoption of low carbon technologies. Using secondary data collected on offshore wind turbines and electrically powered vehicles, the analysis allows determining the actual quantities of rare earths used within permanent magnets and batteries. The results of this paper disprove the widespread allegation that availability risk impedes deployment of offshore wind. Contrary to this, a potential supply shortage would disrupt the further development of the automotive industry and its electrification.

Introduction

Within the past couple of years, growing concerns over massively skewed world production and supply of rare earths have emerged in the specific context of clean energy technologies. On the one hand, the supply risk arises from an institutional inefficiency of the market. Despite the fact that China is currently the largest rare earths producer globally with a market share of 89%, and at the same time possesses single largest reserves, concentration per se is not the main driver of supply disruption. Instead, it is China’s protectionist policies in light of its national interests of industrial upgrading which substantially distort the market 1. On the other hand, the increased adoption of low carbon technologies, driven by institutional settings such as the EU’s Strategic Energy Technology Plan (SET-Plan), as well as by industrialisation effort of developing countries 2, require stable supply of rare earths. This growing imbalance between increased demand and tighter supply implies that while low carbon technologies are intended to tackle climatic changes, their deployment seems to be adversely affected by resource scarcity. The question arises then to what extent do potential supply shortages of rare earths pose barriers to the deployment of latter.

The aim of the present paper is to examine the specific case of offshore wind turbines and alternative technology vehicles - the two technologies which were identified by scientific literature as major drivers of change in rare earths demand, and which are
often incorrectly claimed by headlines of newspaper articles as impossible to be manufactured without rare earths content. In fact, several forecasts by national and international organisations drawn up recently, acknowledge the source of supply risk as being the rapid increase in consumption and China's export policies \(^3\)\(^-\)\(^7\). Along these lines, \(^8\) construct demand scenarios of rare earths originating from production of wind turbines and electric vehicles. However, these usage projections underlie many simplifications and assumptions that do not depict the status quo of technology. Consequently, \(^9\) attempts to determine quantitative shares for HDDs, mobile phones, wind turbines and electro mobility in rare earths permanent magnets. While the author offers a realistic picture on the former two using primary data analysis, his estimates prove incomplete for the latter two. In fact, he only considers permanent magnets in electric traction drives, disregarding those present in other parts of a vehicle (e.g. sunroofs and automatic door locks), what leads to an underestimation of their respective demands for rare earths. Similarly, batteries are not taken into consideration. Moreover, figures are based on vehicles' sales in Germany and the US only. In this light, the present paper estimates global sales data on both energy and car maker/model levels globally, what allows drawing more robust conclusions. In terms of wind turbine technology, at present no analysis exists on the content of rare earths used within offshore wind.

**Methods**

The analysis is carried out by first compiling an overview of various topologies of generators, electric motors and batteries. For this purpose, specialised engineering literature was analysed. Second, in order to determine the quantities of rare earths used in offshore wind, all offshore wind farm projects (i.e. deployment phase of a farm) were screened globally. Data was collected for fully and partially commissioned projects, as well as for those under construction in 2014, from dedicated online databases and news portals on offshore wind \(^10\)\(^-\)\(^15\) and subsequently enriched with information on generator designs from manufacturers' websites. Projects under construction where turbine types were not publicly announced were omitted. Similarly, for electrically powered vehicles, data was collected from manufacturers' websites and specialised online portals \(^16\)\(^-\)\(^20\) for all models in production by end of 2014. Only passenger cars were taken into account. Buses, heavy duty vehicles, motorcycles and three-wheelers are not within the scope of this analysis. Also, vehicles in prototype or pre-production stages and those not mass produced were excluded, while discontinued models were kept. Since global sales figures broken down to car maker/model levels are not publicly available, an estimation was carried out based on information gathered from various sources \(^21\)\(^-\)\(^31\) and from respective car manufacturers' websites.
Offshore Wind Turbines

The central priority of the SET-Plan is to create a low-carbon economy and wind power is one of the technologies foreseen to contribute to this transition\(^6\). Wind is the fastest growing renewable energy source, having increased 8-fold over the past 10 years \(^3^2\). But limited space for further development of wind energy onshore, availability of higher wind speeds as well as opportunities to launch industrial wind projects of magnitudes parallel to power stations, led to progressive siting of wind turbines offshore \(^3^3\). In line with this, recent R&D projects are focusing on challenges primarily in offshore technology. In terms of drive train innovations, the focus lies on improvement of reliability of gearbox and on development of direct drive and hybrid drivetrain technologies. In essence, the main difference between these lies within their drivetrain designs, which in turn influence the requirement for rare earths. The detailed discussion on respective topologies can be found in \(^1\) and has also been summarised in the Table 1.

Table 1: Generator types in wind turbine technologies and their respective permanent magnet and rare earths contents.

<table>
<thead>
<tr>
<th>Wind Turbine</th>
<th>Gearbox</th>
<th>Generator</th>
<th>Permanent Magnet</th>
<th>Rare Earths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geared Drivetrain</td>
<td>Single Stage</td>
<td>Induction (IG)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Multi-Stage</td>
<td>Wound Rotor Induction (WRIC)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mixed Cage (SCIG-MC)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Doubly Fed Induction (DFIG-MG)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Direct Drive</td>
<td>Electrical Excited Synchronous (EESG-DD)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Permanent Magnet Excited Synchronous (PMSG-DD)</td>
<td>650 kg/MW</td>
<td>250 kg/kW (Nd, Dy, Pr, Tb)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High Temperature Superconducting (HTS)</td>
<td>-</td>
<td>YBCO: 3.1 kg/kW (Y, La, Ce)</td>
<td></td>
</tr>
<tr>
<td>Hybrid</td>
<td>Single-Stage</td>
<td>Permanent Magnet Synchronous (PMSG-SS)</td>
<td>100 kg/MW</td>
<td>25 kg/kW (Nd, Dy, Pr, Tb)</td>
</tr>
<tr>
<td></td>
<td>High Temperature Superconducting (HTS)</td>
<td>-</td>
<td>YBCO: 8.02 kg/kW (Y, La, Ce)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Multi-Stage</td>
<td>Permanent Magnet Synchronous (PMSG-MC)</td>
<td>80 kg/MW</td>
<td>25 kg/kW (Nd, Dy, Pr, Tb)</td>
</tr>
</tbody>
</table>

On the one extreme, traditional geared designs – with squirrel cage generators (SCIG) or with doubly-fed induction generators (DFIG) \(^3^4\) – are rare earths free. On the other extreme, while gearless direct drive machines contain no rare earths if excited by electromagnets (electric excitation synchronous generator (EESG-DD)), when designed with permanent magnets (permanent field excitation generators (PMSG-DD)) these turn very rare earths intensive. In fact, some 650 kg/MW of magnets are used in these
machines, with a rare earth content of 250 kg/MW\textsuperscript{35,36}. Note that there is a lack of consensus on permanent magnet content within these generators, opinions ranging from 500-625 kg/MW\textsuperscript{37}, through 600-800 kg/MW\textsuperscript{38}, up to 1000 kg/MW reported by various consultancies. Hybrid drivetrains, containing a single-stage (PMSG - SG) or a two-stage gearbox (PMSG - MG) combined with a medium speed permanent magnet generator\textsuperscript{33}, represent a compromise between the two standards. Their substantially smaller magnets with 160 kg/MW and 80 kg/MW respectively, contain up 10 times less neodymium, dysprosium, praseodymium and terbium per MW of power produced compared to PMSG-DD machines\textsuperscript{39,40}. Finally, High Temperature Superconductor (HTS) technology utilises minute quantities of yttrium, lanthanum and cerium within its YBCO conductors - the latter two being the most abundant rare oxides\textsuperscript{41,42}.

By end of April 2014, a total of 99 offshore wind projects has been operating 2'463 turbines and producing 7.62 GW of offshore wind power globally. Following observations stand out: in terms of capacity generated, the most widely spread design is the conventional geared drive train with SCIG, which together with DFIG make up 96% of current offshore market. Permanent magnet driven technology lags significantly behind covering the remaining market share of 4%, with an equal split of 2% between direct drive and hybrid generator designs. In terms of the distribution of generator types across projects, 16% of all commissioned projects make use of permanent market drivetrain technology. This can be explained by the fact that many of these turbines are currently at prototype stage and are being tested in low numbers at various test sites. Finally, average power range of generator types is illustrated in Figure 1 (left). While conventional geared drive train designs have similar average powers of 2'881 MW for SCIG and of 2'766 MW for DFIG, this is substantially higher for PMSG topologies with 3'447 MW in aggregate. The average of 4'500 MW for EESG-DD is to be interpreted with caution since currently there is only one turbine deployed offshore worldwide. Having said this, one can conclude that PMSG drivetrains, though with currently lower market share, tend to be deployed within larger power range turbines. While the UK is the leader in total installed offshore capacity, followed by Denmark and Germany, by far the most permanent magnet driven machines are at present deployed offshore in China.

Accounting for projects under construction in 2014, in addition to those already commissioned, the capacity generated increases by more than half to 12.72 GW and number of turbines increases to 3'871. Share of PMSG turbines increases to 16% of total capacity, with shares of hybrid models increasing to 5% and 6% for PMSG-SG and PMSG-MG respectively, while share of PMSG-DD increases to 5%. Furthermore, share of projects relying on permanent magnet driven technology increases to 21%. Figure 1 (right) indicates that the average power range of permanent magnet excited direct drive machines increases slightly to 3'621 MW and the total capacity produced
increases by 600% - from currently 284 MW to 2’000 MW of produced power once these projects turn fully operational. At the same time, increase in geared drivetrains remains below 50%. Market share of electrically excited generator technology remains unchanged. To summarize, there is acceleration in deploying permanent magnet drivetrains in the near future, at the expense of traditional geared technologies. This trend is predominantly driven by Germany which is planning to add 600 MW of power produced by PMSG turbines offshore, followed by China and the UK with 464 MW and 436 MW respectively, and Belgium with half as much additional power produced at full commissioning of projects. While European countries will be installing only hybrid drives, half of added MW in China will be produced by direct drive generator wind turbines.

![Figure 1: Generator designs in global offshore wind projects: commissioned (left); commissioned and under construction in 2014 (right).](image)

In terms of quantities of rare earths used, assuming contents as indicated in Table 1, 108 tonnes of permanent magnet and 40 tonnes of rare earths have been used for all currently commissioned offshore wind farm projects so far. For all newly installed turbines in projects under construction, manufacturing of generators required 430 tonnes of permanent magnets, the rare earths content of which was slightly more than 150 tonnes. On the one hand, this represents an increase in demand for rare earths by approximately 380%, while on the other this constitutes less than half a percent of respective neodymium and dysprosium supplies forecasted for 2014. In general, future expansion of offshore wind is tied to regulatory stability, as well as to existence of cable routes and high voltage transmission lines linking offshore wind farms to mainland grid. Penetration of PMSG topologies in particular, will depend on availability risk and pricing volatility of rare earths on the one hand, and competition from alternative technologies on the other.
Advanced Technology Vehicles

Besides reduction of greenhouse gases' emissions, another main line of argumentation in favour of advanced technology vehicles is the reduction of importer countries' dependence on foreign oil. The question remains though, to what extent does the technology shift from internal combustion engine to advanced technology vehicles expose us to dependence on rare earths.

Based on the level of hybridisation, modern vehicles can be classified into internal combustion engine vehicles (ICEV), hybrid electric vehicles and all-electric vehicles (AEV) \(^{43}\). The latter two can be further broken down based on energy sources used into battery, fuel cell and solar energy models. The latter two technologies are still in early stages of development and hence are not in the scope of the present analysis. Battery electric vehicles (BEV) are propelled entirely by battery packs, while full-hybrid vehicles (HEV) run on fuel alone, and plug-in hybrids (PHEV) use the combination of gasoline and electric motors \(^{43-45}\). An overview is provided in Table 2. One thing all advanced technology vehicles have in common is the electric motor in their drivetrains. An overview of main motor design drives together with their specifications and comparison of performance is provided by \(^{46}\). In short, the most common design is the permanent magnet motor with currently more than 80\% of market share, as compared to the induction motor with a market share of 11\% only \(^{47}\). Just like in wind turbines, magnets in electric motors contain neodymium, dysprosium and traces of praseodymium and terbium. It has been estimated that the electric traction drive contains some 0.6 kg of rare earths \(^{48}\).

The case of batteries is somewhat different in that several battery technologies co-exist on the market. An overview of secondary battery systems is reported in \(^{43, 49-53}\). Battery technologies currently used in respective vehicle energy models are discussed in \(^{1}\) and also summarised within Table 2. In short, besides the two most widespread designs - nickel metal-hydride (NiMH) and lithium-ion (Li-ion) - other battery technologies exist on the market: nickel-cadmium (Ni-Cd) and lead acid (PbA) (outdated); zinc-air (Zn-air), lithium-sulphur (Li-S) and lithium-iron phosphate (LFP) (under development); and Zebra and lithium-metal-polymer (LiPo) (unproven viability). However, currently only the NiMH battery contains rare earths, its negative electrode being made of hydrogen absorbed in metal alloy of the type MN(Ni,Co,Al,Mn)\(_5\). Such batteries contain up to 10\% mischmetal (MN), made up primarily of lanthanum and to some lesser extent of cerium, neodymium and praseodymium, as well as of metallic impurities \(^{51, 54-57}\). In fact, their large usage of rare earths - 3.5 kg as estimated by \(^{48}\) - was one of the reasons why rare earths free lithium battery technology started to catch up.
**Table 2:** Vehicle technologies classified by hybridisation and their respective rare earths contents.

<table>
<thead>
<tr>
<th>Hybridisation</th>
<th>Energy Models</th>
<th>Propulsion (Rare Earths)</th>
<th>Powered by</th>
<th>Battery (Rare Earths)</th>
<th>Other (Rare Earths)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal Combustion Engine Vehicle (ICEV)</td>
<td>ICE Vehicle</td>
<td>Gasoline or Diesel Engine (-)</td>
<td>-</td>
<td>-</td>
<td>0.22-0.44 kg: Nd, La, Ce, Pr, Dy, Ta</td>
</tr>
<tr>
<td>Hybrid Electric Vehicle*</td>
<td>Full-Hybrid Electric Vehicle (HEV)</td>
<td>Gasoline Engine and Electric Motor (0.6 kg: Nd, Dy, Pr, Tb)</td>
<td>NiMH (3.6 kg: Nd, La, Ce, Pr); Li-ion, LiFe, PbA (-)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plug-In Hybrid Electric Vehicle (PHEV)</td>
<td>-</td>
<td>NiMH alone (0.6 kg: Nd, Dy, Pr, Tb)</td>
<td>Li-ion, LFP (-)</td>
<td></td>
</tr>
<tr>
<td>All-electric Vehicle (AEV)</td>
<td>Battery Electric Vehicle (BEV)</td>
<td>Electric Motor Alone (0.6 kg: Nd, Dy, Pr, Tb)</td>
<td>Battery</td>
<td>Li-ion, LFP, PbA (-)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fuel Cell Vehicle (FCV)</td>
<td>-</td>
<td>Hydrogen</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Photovoltaic Cell Vehicle (PCV)</td>
<td>-</td>
<td>Sunray</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2 (left) summarises the shares of individual designs adopted by car manufacturers within their vehicles. NiMH batteries are employed within nearly a third of currently available advanced technology vehicle models, what makes them the second most deployed battery technology. However, when looking at the breakdown of uses across specific vehicle energy models as illustrated in Figure 2 (right), it becomes obvious that the latter are only used within HEV. The reason behind are limitations in specific power and energy densities, as well as lack of scalability with respect to its size. In fact, while HEV are propelled by both ICE and electric motor, in BEV and to some extent in PHEV it is the battery which powers the electric drivetrain and hence higher performance of the former is required. This makes NiMH batteries less suitable to be deployed in the latter two

In terms of rare earths quantities used, claim Toyota Prius to be the most rare earths intensive consumer product ever made with its 11 kg of rare earths content. However, other sources are more moderate with their estimates ranging from 2.17 kg to 2.45 kg of rare earths in Prius II batteries alone. Finally, according to estimates by a hypothetical mid-size HEV with a nickel metal hydride battery, contains 3.5 kg and 0.6 kg of rare earths within its battery and electric motor respectively, and another up to 0.44 kg scattered across over 700 vehicle parts. Note that this estimate decreases to half when considering rare earths content in basic vehicles in developing countries on the one hand, and that this quantity is contained in all conventional ICEV, for example as small magnets contained in sunroof and automatic door locks, or in catalytic converter. Two thirds of this quantity is estimated to be made up of
neodymium and 6% of dysprosium. As negligible as these quantities sound across single vehicles, for the total of 87.25 million vehicles produced globally in 2013, 29,700 tonnes of rare earths elements were used based on the above assumptions. This quantity when converted into REO content constitutes 31% of global rare earths supply for 2013. In terms of individual rare earths, approximately 70% and 120% of forecasted global neodymium and dysprosium supplies for 2014 are consumed. Considering tighter supply estimated for 2016, respective consumptions would increase to 80% and 210%.

**Figure 2:** Battery technologies deployed: in advanced technology vehicles (left); across vehicle energy models (right)

For 2013, estimates on global vehicles’ sales indicate that HEV are dominating the market with a global share of approximately 86%, while respective shares of PHEV and BEV are 6% and 8%. Based on data collected on battery technologies and on sales figures it was possible to determine that NiMH batteries currently have an approximate market share of 75% of all HEV. This implies that, electric motors and batteries in electrically powered vehicles require 723 tons and 3,413 tons respectively, what represents an additional 4% of global rare earths supply in 2013. Based on individual supplies forecasted for 2014, the shares of neodymium, lanthanum and dysprosium are 4%, 5% and 14%, respectively. Considering the growing deployment of electrically powered vehicles projected to reach annual global sales of 6.1 million by 2023, these alone would require 18% of current annual rare earth’s production. This is an approximation and only holds when assuming that global production stays the same, as well as market share of NiMH batteries and of rare earths permanent magnet motors remains unchanged, and that no minimisation takes place. In general though, there is a substantial uncertainty in deployment trends of energy models and of their charging infrastructures. These depend on incentives and regulations by governments, as well as on fuel prices. Additionally, price decreases envisaged for Li-ion battery packs and potential price volatilities and availability risk of rare earths might speed up the paradigm shift towards the former.
Impact of Rare Earths Price Volatility on Low Carbon Technologies’ Producers

Though China has been dominating the rare earths market since mid-1990s and export and production quotas were in place already in early 2000s, the rare earths problematic has only become a prominent topic in recent years. One of the reasons behind are the small quantities of rare earths used in single technologies, as well as the largely inelastic demand. Moreover, since rare earth prices are rather low relative to the total cost of the final product, changes in prices did not have substantial impact on producer costs. However, price hikes like those in 2010-2011 called innovation of direct drive turbines in question, despite them being a superior technology on open sea\textsuperscript{65-67}. For illustration, assuming a PMSG-DD with rated power of 2 MW, rotor diameter 82 m and hub height 80 m, and following the manufacturing cost breakdown according to components as specified by \textsuperscript{33}, cost of 80 USD/kg of required quantity of permanent magnet constitutes 23\% of generator costs and 6\% of total component costs. Assuming a variation of prices of permanent magnet up to 420 USD/kg during the rare earths crisis in 2011 \textsuperscript{68}, this increases the share of permanent magnet costs to almost 2/3 of the cost of generator and a quarter of cost of all components. This in turn increases the cost per kW by 50\% relative to competing DFIG gearbox technology with same parameters. Consequently, uncertainty about high and volatile prices and threat of supply risk of rare earths is inducing producers to adjust the designs of their drivetrains. For example, within the EU project on developing a 20 MW wind turbine (INNWIND), while its predecessor (UPWIND) considered conventional drive train optimisation, the new project is to focus on superconductive and magnetic pseudo direct drive generator (PDD) which integrates a low ratio magnetic gear thanks to which the substantial size and cost of conventional direct drive generators are eliminated \textsuperscript{69-71}.

For what concerns raw material costs in advanced technology vehicles, according to the component cost comparison \textsuperscript{47}, the cost of a 50 kW permanent magnet electric motor is by 30\% - 200\% higher than that of a 50 kW copper rotor induction motor, depending on the pricing of rare earth magnets. Indeed, substantial price swings and uncertainty about stable supply of rare earths spurred R&D on induction electric motors by some car manufacturers \textsuperscript{72-75}. Others are developing electric motors with reduced amounts of dysprosium \textsuperscript{76-78}. Also, Hitachi has been developing a prototype of a motor using amorphous metal for iron cores and ferrite magnets as rotors \textsuperscript{79}, while Hybrid Electric Vehicle Technologies has patented switched reluctance motor which eliminates use of rare earths by ferromagnetic magnet rotor \textsuperscript{80}. Batteries instead, constitute the most expensive part of electric vehicles - ranging from a third to over a half of HEV’s component cost. The cost of rare earths used within a NiMH battery, when converted into rare earths mischmetal composed of 63.0 wt.\% La, 17.4 wt.\% Ce,
10.7 wt.% Pr, 2.2 wt.% Nd and 6.7% others, increased substantially from 21 USD on 30/12/2005 to 121 USD on 18/04/2014. Considering metal prices as of end of June 2011 when rare earths crises peaked, the estimated cost of total rare earth content increased by 3300% when compared to 2005 year-end. Nonetheless, during the time of higher prices producers presumably use up their private stocks so as to mitigate temporary price hikes. Currently, there seems to be a paradigm shift ongoing from NiMH to lithium technology, which despite its higher production costs is cheaper in terms of materials used. As an example, Ford has been switching away from NiMH battery in its earlier Escape model to Li-ion battery in its Fusion and C-MAX models. Finally, the quantities of rare earths contained in regular ICEV remain a serious issue in the coming years. Nevertheless, it is expected that in the long run these can also be replaced by other materials resulting from basic research initiatives as discussed in \(^1\).

**Conclusions: Separating Myth from Reality**

This paper examined the role of rare earths supply risk in the specific context of low carbon technologies deployment. The results disprove the widespread allegation that availability risk of rare earths impedes deployment of offshore wind per se. Contrary to this, the deployment of permanent magnet technology in particular might become prone to supply risk, depending on its future market share and level of hybridisation adopted. While its share of total capacity produced is currently on increase, its share of annual global supply of rare earths is negligible. The automotive market and its electrification instead, are substantially dependent on availability of rare earths. They required over a third of the global rare earths production in 2013 and the share is expected to increase further with growing deployment of both conventional ICEV and electrically powered vehicles. Therefore a potential supply disruption would impede further development of the market altogether.

To conclude with, uncertainty about volatile prices and threat of supply shortages induce manufacturers to shift away from technologies containing rare earths, and ultimately render innovation in the latter economically non-viable. In the face of increasing demand for these, it might follow that manufacturers, and thus all their innovation activities, relocate to China with view of sourcing cheaper inputs at stable supply. Consequently, it becomes imperative for policy makers to design policies in order to avoid getting the world “trapped” in the rare earths dependence. In this light, concerted action should be directed towards R&D on material substitution within permanent magnets, on increasing efficiency of rare earths recycling and on developing sustainable mining and processing techniques. It remains to be seen whether China’s distortive industrial policies will be abolished following the recent resolution on the WTO dispute.
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EXPLORING RARE EARTHS SUPPLY CONSTRAINTS FOR A FULL GLOBAL PENETRATION OF RENEWABLE ENERGY: CASE OF WIND TURBINES AND ELECTRIC VEHICLES

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Abstract

The dependency on critical resources like Rare Earth Elements (REEs) has been pronounced as a potential barrier to a broader implementation of emerging renewable energy technologies. This study explores the dependency of such technologies especially wind turbines and electric vehicles along with other background end-uses on two key REEs, i.e. neodymium (Nd) and dysprosium (Dy). Our study reveals that a highly accelerated rate of REEs mining is unavoidable in order to keep up with the pace of increasing demand from new technologies required in a renewable energy strategy for meeting the climate change challenge. Recycling does not seem to be in a position to close the wide gap between future demand and supply by 2050 mainly due to the long lifetime of key end-use products.

Introduction

The Rare Earth Elements (REEs) consist of 15 elements from the Lanthanide series plus two more elements namely scandium and yttrium. This group is the largest chemically coherent group in the periodic table, and all the elements are found together in geologic reserves. These elements have similar chemical characteristics, which on one hand allow them to substitute for each other in their final application but on the other hand make their separation and refinement to pure metal a very difficult process. REEs have unique physical and chemical properties which make them highly attractive in many of today’s hi-tech applications e.g. permanent magnets having Neodymium (Nd) and Dysprosium (Dy) are widely used in computers, audio systems, electric and hybrid vehicles, cell phones, wind turbines, Magnetic Resonance Imaging (MRI) machines, and others. The performance level provided by these magnets is currently unmatched with any other available magnets, which makes these elements highly attractive for
the above mentioned technologies in order to get the same high level of performance.

The wind turbines and Electric Vehicles (EVs) are the two key emerging clean energy technologies, which are considered highly promising in order to reduce our dependency on fossil fuels as well as greenhouse gas (GHG) emissions. However, the full global penetration of these clean energy technologies in future may be constrained by the possible supply restrictions of REEs. REEs are considered as critical resources by a number of studies, mainly because of the monopoly situation, i.e. what China currently supplies more than 85% of the REEs production. The remaining is supplied by Australia, USA, India, Brazil, Malaysia, and other countries. During the recent years, China has reduced the export of REEs to the rest of the world in order to prioritize the domestic demand, and to increase the production and export of high value goods using REEs e.g. permanent magnets, motors, and batteries. Due to the introduction of export quota by the Chinese Government, the prices of REEs skyrocketed in 2011. This sharp increase in price led the stakeholders to seek some other solutions e.g. investing in mines outside China, substituting REEs by some other elements and increasing the recycling rates.

The current study addresses the issue of possible future supply constraints of Nd and Dy for the emerging clean energy technologies as well as other potential end-use sectors. The aim of this study is to explore the risk of potential supply constraints considering the predicted high demand of Nd and Dy and their forecasted supply by 2050. In order to reach the aim, an ultimate renewable energy scenario is developed to show the future demand of Nd and Dy, not only for the wind turbines and EVs but also for other end-use sectors such as computers, audio systems, industrial motors, and others. Simultaneously, a historical trend based projected scenario is developed regarding the primary production of Nd and Dy up to 2050 in order to check if the demand will outstrip supply. Moreover, different recycling efficiencies for various end-use sectors have been assumed to investigate the effect of secondary production on the demand and supply of Nd and Dy.

**Materials and Methods**

**Demand scenario**

In order to reveal the potential supply constraints of REEs for the emerging clean energy technologies, an ultimate renewable energy scenario is modelled and assessed in this study. To estimate the demand of Nd and Dy by wind turbines, it is important to model the global electricity demand by 2050, the share of electricity produced by
wind turbines and the market penetration rate of direct-drive wind turbines as these turbines are so far dependent on the strong permanent magnets containing Nd and Dy. Table 1 shows the required share of wind power as well as the market share of direct-drive wind turbines in order to meet the ultimate renewable energy scenario by 2050. Table 2 presents the share of EVs sold by 2050.

**Table 1: Overview of the Ultimate renewable energy scenario and the share of wind power produced by direct-drive wind turbines up to 2050**

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Total Electricity demand (TWh)</th>
<th>Share of Renewable energy (%)</th>
<th>Share of wind power (%)</th>
<th>Wind Power demand 2050 (TWh)</th>
<th>Market penetration rate of direct-drive wind turbines up to 2050 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate Renewable Energy</td>
<td>37,656</td>
<td>100</td>
<td>33</td>
<td>12,426</td>
<td>50</td>
</tr>
</tbody>
</table>

**Table 2: Overview of EVs deployment in the Ultimate renewable energy scenario**

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Passenger vehicles by 2050 (million)</th>
<th>Sales of passenger Vehicle in 2050 (million/year)</th>
<th>Market penetration rate of EVs by 2050 (%)</th>
<th>Sales of EVs in 2050 (million/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate Renewable Energy</td>
<td>1800</td>
<td>170</td>
<td>100</td>
<td>170</td>
</tr>
</tbody>
</table>

For all the other end-use sectors such as electric bicycles, computers, audio systems, medical applications etc., an annual growth rate of 4% is considered until 2050. Furthermore, the amount of Nd and Dy for direct-drive wind turbines is considered to be 150 and 14 Kg MW⁻¹ respectively. For EVs, the amount of Nd and Dy per vehicle is 0.62 Kg of Nd and 0.09 kg of Dy. In this study, the average lifetime is considered to be 20 years for wind turbines, 10 years for EVs and 10 years for all the other background end-uses.
Supply scenario

In the current study, both primary and secondary supply of Nd and Dy have been modelled up to 2050, where primary supply refers to the mine production whereas secondary supply refers to the supply of Nd and Dy from recycling of end-of-life products. The primary supply of Nd and Dy has been projected following the historical production trend of REEs from 1994 to 2014. The secondary supply has been modelled assuming 90% recycling rate for wind turbines, 70% for EVs and 40% for other background end-uses at the end of their lifetimes (as mentioned earlier) by 2050.

Results and Discussion

Figure 1 presents the demand and supply (primary and secondary) comparison of Nd and Dy by 2050. Results show that the annual total demand of Nd reaches from almost 16 Gg in 2007 to approximately 242 Gg in the ultimate renewable energy scenario by 2050. It can be noted that wind turbines do not seem to be the major end-user of Nd compared to other end-use sectors especially EVs by 2050. Same trend can be visualized in case of Dy, where annual total demand of Dy rises from nearly 1.8 Gg in 2007 to approximately 32 Gg in the ultimate renewable energy scenario by 2050. Here again, EVs appear to be the major end-users of Dy followed by other end-uses.

As Figure 1 reveals, the Business As Usual (BAU) projected primary supply is not likely to be enough to support the forecasted demand by 2050. In case of Nd, the gap between the forecasted future demand and supply is 77% in the ultimate renewable energy scenario. Moreover, the results clearly show that the linear trend based projection of Nd mining is not likely to be enough to meet the increasing demand even in short (2020) to medium term (2030). The same results can be visualized for Dy, where it becomes evident that the BAU projected primary supply seems to meet only 16% of the projected demand in the modelled ultimate renewable energy scenario by 2050.

Furthermore, Figure 1 shows the potential role of recycling in lowering the future demand of Nd and Dy. It becomes clear that recycling seems to reduce the gap between supply and demand from 77% to 55% for Nd by 2050. For Dy, it becomes evident that recycling can help in reducing the gap between forecasted demand and supply from 84% to 60% in the modelled scenario by 2050. The reason why recycling is not likely to meet a considerable share of demand by 2050 is because of longer lifetimes of products, which delays the recovery of resources from the post-consumer applications.
Figure 1: Overview of the forecasted demand and the projected primary and secondary supply of Nd (upper) and Dy (lower) in the Ultimate renewable energy scenario by 2050, where the bars present demand and the slopes present the supply of Nd and Dy.

Conclusion

From the results presented above it can be concluded that the historical trend based projected primary supply of Nd and Dy is not likely to meet the forecasted high demand of these resources by 2050. Recycling does not seem to play significant role in reducing the gap between demand and supply of Nd and Dy by 2050, primarily due to the long lifetimes of key end-use products such as wind turbines and electric
vehicles. A highly accelerated rate of REEs mining is unavoidable in order to keep up with the pace of increasing demand from new technologies required in a renewable energy strategy for meeting the climate change challenge.

References
MATERIAL FLOW ANALYSIS FOR IDENTIFYING NEOODYMIUM FLOWS AND STOCKS AND RECYCLING POTENTIALS IN THE EU-28

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Abstract

This paper addresses the material flow analysis (MFA) of Neodymium (Nd) in the EU-28. Due to their recycling potential, the Nd applications considered in this study are permanent magnets and nickel-metal hydride batteries. Flows and stocks of Nd are considered all along the value chain within the EU, from the import of concentrates containing Nd, Nd purification and metal production, manufacture of magnets and batteries, use of products in the economy, and finally the management of end-of-life products. The synthesis of this wealth of information in the form of Sankey diagrams provides a holistic vision of the dynamics of Nd within the EU economy. An innovative aspect of the project compared to existing MFAs is the incorporation of lithospheric stocks of continental Europe in the analysis.

Introduction

On February 2011, the European Commission adopted a strategy document which sets out targeted measures to secure and improve access to raw materials for the EU¹. Based on a three-pillar approach, it aims at improving access to raw materials for Europe by (1) fair and sustainable supply of raw materials from international markets, (2) fostering sustainable supply within the EU, (3) boosting resource efficiency and promoting recycling. In this context, the Commission identified 14 minerals as critical for the economy ² based on their risk of supply interruption. Rare Earth elements (REEs) were among these identified critical raw materials.

A comprehensive data inventory of the material flows in industry and society is essential to get the solid ground for informed discussion and decision making on the supply of raw materials. Such data provide information on the quantity and quality of raw materials in each stage or phase of the flow. This allows more decisions that provide balanced, secure and sustainable supply throughout the entire material flows.
The on-going ASTER project, started in 2012 for a period of three years, aims at applying material flow analysis (MFA) to selected rare earth elements (REEs) for the EU-28. Certain rare earth elements are deemed “critical”\(^3\), as they combine importance for strategic sectors of the economy with risks of supply shortage\(^2\). The recent JRC report\(^3\) identifies six critical REEs (Dy, Eu, Tb, Y, Pr and Nd) that are precisely the REEs that were selected for the ASTER project.

While the paper by Guyonnet et al. (this conference) focuses on the REEs in phosphor lamps (Tb, Eu, Y), this paper addresses REEs contained in permanent magnets and NiMH batteries, i.e. Nd, Pr and Dy.

**Description of the studied system**

For the case of permanent magnets and NiMH batteries, the two systems that were analysed are described schematically in Figures 1 and 2. These figures illustrate a certain number of processes with, starting upstream in the value-chain: separation (S) of rare earth concentrates, fabrication (F) of NdFeB alloy (for permanent magnets) or LaNiM\(_5\) mischmetal alloy (for NiMH batteries), manufacture (M) of permanent magnets or NiMH batteries, insertion of these products in applications (A) such as cars, computers, cell phones, wind turbines, etc. – only for permanent magnets, use (U) of these applications in the economy, waste management (WM) of end-of-life products and final elimination (landfill and/or dissipation in the environment). These various processes are linked by arrows that represent flows from one to another. Differences between flows into or out of a process imply an addition or subtraction to stock within the process. The dashed line in Figure 1 and 2 represents the limits of the studied system (the EU-28). An additional “process” appears in Figure 1 and 2 indicated as “L” (lithosphere). The lithosphere represents geological potentialities in the form of REE resources (as opposed to reserves\(^5\)). For geological and economic reasons, the limits of this process were taken as continental Europe (including the Scandinavian shield and the Kola Peninsula) plus Greenland.
Figure 1: Schematic illustration of the system investigated in the case of permanent magnets

Figure 2: Schematic illustration of the system investigated in the case of NiMH batteries
Flows were calculated for the year 2010, taken as the reference year of the study and estimated over a number of years exceeding the expected average lifetime of the considered products (taken as, e.g., 7 years for a NiMH portable battery, 3 years for a laptop, and 13 years for a car), in order to obtain estimates of in-use stocks and end-of-life product flows.

**Information sources**

Information sources are the same as those described in Guyonnet et al. (this conference). They include Eurostat trade and production data, as well as literature data such as specialised reports on rare earth elements\(^5\), \(^7\), USGS data\(^8\), company reports on product sales, etc. Expert knowledge has been used to fulfill data gaps. For the evaluation of geological potentialities in the lithosphere, over 350 deposits or occurrences located within the EU-28 were analysed\(^9\), considering mineralogical characteristics of these deposits and occurrences.

**Some results to-date**

As the ASTER project is still on-going, the results presented herein are preliminary and only describe qualitatively the Sankey diagrams elaborated for Nd in permanent magnets and NiMH batteries.

Flows and stocks of Nd were calculated for each step of the value chain of permanent magnets and NiMH batteries.

The method to assess the quantities of produced and traded (imported and exported) rare earth oxide mixtures (REOs) in EU-28, based on the customs data has been described by Guyonnet et al. (this conference). With respect to the upstream portion of the value chain, the same HS codes were used as in the Öko-Institut report\(^7\) (see Table 1 of Guyonnet et al., this conference). GTA data for Chinese exports based on 8-digit HS codes were also used. These HS codes represent raw products that contain mixtures of REEs. In order to obtain data on individual REEs, a disaggregation method was applied\(^10\). The method considers the relative market shares of products containing REEs (e.g., auto catalysts, magnets, batteries, polishing powders, etc.) and the composition of the REE mixtures in each product.

Application of this disaggregation methodology to these data provides information relative to flows F2, F3 and F4 of Figure 1, and F1, F2 and F3 of Figure 2. Expert judgement used to check the consistency of the calculated flows with the industrial reality was provided by SOLVAY, a major player of the separation industry in Europe. In Europe, separation of Nd for magnet applications is performed by SILMET in Estonia.

The Fabrication step involves the production of the NdFeB alloy for permanent magnets and the LaNiM\(_y\) mischmetal for NiMH batteries. The Manufacture step involves the production of the NdFeB permanent magnets and the NiMH batteries.
Information relative to imports and exports of NdFeB alloy and NdFeB magnets is obtained based on HS codes 85051100 (Permanent magnets of metal and articles intended to become permanent magnets after magnetization, excl. Chucks, clamps and similar holding devices) and 85051990 (Permanent magnets and articles intended to become permanent magnets after magnetization, of materials other than metal or agglomerated ferrite). Expert information was necessary to disaggregate the quantities traded under these codes that regroup both alloys destined to permanent magnet production and permanent magnets, the market shares of NdFeB magnets within permanent magnets (in and out of the EU), and the typical composition of these products.

Imports, production and exports of NiMH batteries were quantified on the basis of Eurostat data for portable and industrial NiMH batteries (HS code 85078020: Nickel-hydrid accumulators; ProdCom code 31402383: Nickel-hydrid accumulators) and on literature data for NiMH batteries contained in electric and hybrid vehicles.\(^6\) Further down the value chain (Application step and Use step), data was collected for manufactured products containing permanent magnets and NiMH batteries. The following applications were considered concerning permanent magnets-containing products: electric and non-electric car, laptop and desktop, cell phone, hard drive, washing-machine, refrigerator, air-conditioner, scanner, fax and printer, shaver and little electric equipment, camera, CD players, headphones and earphones, RMI, and wind turbines. Information about production and trade of these products, as well as Nd content and market shares was obtained in specialised or company reports.\(^6\) \(^12\) \(^13\) \(^14\) \(^15\) \(^16\) \(^17\) \(^18\)

Results of the analysis suggest that the orders of magnitude of Nd flows in the EU-28 related to permanent magnets and NiMH batteries are on the order of, resp., 700 and 120 tons entering the “Use” process. In contrast with the Sankey diagrams for Tb, Eu, Y (Guyonnet et al., this conference), that are relatively “balanced” all along the value chain, Sankey diagrams for Nd (and Dy) are very imbalanced due to large quantities in imports to the “Applications” and “Use” processes. Taking into account the history of flows into use in the EU-28 over a period exceeding the expected average lifetimes of the NiMH batteries and the permanent magnet-containing products, in-use stocks for Nd in 2010 are estimated as, resp., 17,000 and 600 tons. The annual additions to in-use stock in 2010 are estimated to be resp., +190, and +50 tons/yr for these elements. The flows related to end-of-life products (F17 in Figure 1 and F11 in Figure 2) are also assessed using the expected average lifetimes of the NiMH batteries and the permanent magnet-containing products. The Nd in the waste flow is estimated as 530 tons due to permanent magnets application and 70 tons from battery applications. Those values represent an upper bound of Nd in the waste flow as the market shares or Nd content of the products arriving at end-of-life in 2010 are potentially lower (less Nd in the composition) than the products used in 2010. With respect to flows F12 in
Figure 2 (recycling), there was no recycling of Nd in 2010 in the EU-28. About 100 tons of REEs from mischmetal are recycled each year but Nd is not part of these REEs. As no recycling of Nd was performed in 2010, the Nd contained in the waste flow ends up in landfills or in dissipative uses such as the cement or steel industry.

These figures can be compared to geological potentialities based on the analysis of three important REE projects: the Norra Kärr project in Sweden and two exploration projects in Greenland (Kvanefjeld and Kringlerne). The Norra Kärr project is well advanced and has recently received the authorisation to operate from the Swedish government. We estimate the resource of Nd at this site to be on the order of 33 kt. The potentials of Kvanefjeld and especially Kringlerne are far superior (resp. 750 kt and 3.5 Mt of Nd), however, the likelihood of these projects entering into production is much lower, due in particular to environmental constraints and social acceptability.

**Conclusions**

Results of the on-going ASTER project provide estimates of flows and stocks of certain REEs in the EU-28, considered as critical. This paper addresses the results relative to REEs in permanent magnets and NiMH batteries, while another paper (Guyonnet et al., this conference) addresses Tb, Eu and Y. Detailed results of the ASTER project are currently in the process of being published.

Criticality with respect to Nd has been somewhat relaxed in recent years, with the diversification of supply sources provided by the Mount Weld deposit in Australia and the Mountain Pass mine in the U.S. The preliminary results of the ASTER project show that should one of the projects in continental Europe and Greenland enter the production phase (with Norra Kärr as the most likely candidate), then criticality with respect to Nd will be significantly decreased.

There is potentially more pressure on Dy. However, current efforts with respect to the optimisation of Dy use in magnets and to substitution contribute to reducing such pressure. Also, preliminary estimates of Dy resources for the three projects mentioned above are resp., 12, 64, 710 kt Dy. This should help tackle the forecasted future increase of Nd and Dy consumption due to the development of the European wind turbine farms.

**Acknowledgments**

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Global Pricing Dynamics of the Rare Earths Industry Europe

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Abstract

This research examines the enigma of a market with critical global demand, deliberately controlled geopolitical supply, yet prices which when not depressed are reported as incomprehensible. Scientific interest and funding is dependent on rare earths having a commercial market, so prices are of crucial importance. The results show that regardless of how critical rare earths are, only 5% to 10% are used in defence and aerospace applications, they are almost exclusively used in consumer products, which implies strict price ceilings for components and raw materials. With China supplying 87% of product and 60% of export demand coming from Japan, those two countries essentially define the supply and demand market. Japan primarily manufactures consumer products. The vast majority of demand therefore sits in what is called an elastic market, and the solutions manufacturers use when faced with pricey components in these markets are to find alternative suppliers or to eliminate the need for the components all together. During the search by manufacturers for alternatives, prices usually hike temporarily because it takes time to source alternatives or change production, but then the price settles in a so called shift to a new equilibrium. These dynamics are evident in the historical rare earths market.

Introduction

This economic research was first described on June and July, 2013 on Investointel.com with the subtitle, “Am I the only one who thinks rare earth prices will always be low? 1” The work was updated in June 2014 comparing predictions with subsequent events and amongst others drew the attention of the USA Critical Materials Institute, suggesting that it would be relevant to European strategies.

Elementary economics states that when a commodity is in crucial demand and supply of that commodity is low or restricted, the price goes up. When entering the rare earths sector in 2012 it was clear to the author that few participants had an answer as to why rare earth prices were not high, and they lamented the fact in vocal
frustration².

China has long intended for its essential monopoly of the rare earths elements to allow control of global rare earth prices³. Yet with most of the world’s rare earth production in China and their efforts to manipulate prices through rigorous control of supply, prices continue to drop. China has done everything it can think of, stopping or limiting production, eavesdrop on producers, eradicate pirating and refusing supply to some clients. Every now and then there is a bump and everyone gets excited, but the trend is clear. Rare earths go into energy, space and military sectors, but that accounts for only about 10% of the demand. With China supplying 87% of product (down from as much as 95% with the advent of Lynus and Molycorp) and with as much as 80% of export demand coming from Japan, those two countries, for all intents and purposes, define the supply and demand market.

Japan mainly manufactures consumer products. Regardless of how important rare earths are, they are therefore used almost exclusively in cheap electronic commodities, which have established retail prices and strict ceilings on the cost of components and raw materials. The vast majority of demand therefore sits in what is called an elastic market. An elastic market is one in which high commodity prices are not tolerated. That is because the eventual products are themselves price sensitive, usually consumer products for mass markets.

The two solutions manufacturers use when faced with pricey materials in these markets, are to find cheaper suppliers or to eliminate the need for the material altogether. During the search by manufacturers for these alternative solutions, prices do usually hike for a little while because it takes time to source alternatives or retool production lines, but then the price settles back down again and there is a so called shift to a new equilibrium between supply and demand.

Once this erroneous price manipulation fails, then the manipulator generally changes tack attempting to retain or recapture market share. All of these dynamics are clearly evident in the rare earths market³,⁴.

The results of this research suggest that the rare earths market is entering a final phase, where prices will remain moderate but stable. Business models or projections based on hoped for or sustained high prices are probably doomed, but those companies presenting profits on current prices are probably safe and worth
investigating.

**Rare Earths, Elastic Markets & Sheep**

A global market can sometimes be thought of as a chess game, so when business plans are based on only one side’s strategies, the surprises from the other side can be devastating. Since chess is a game between only two players, a less limiting analogy is a large set of simultaneous chess games, with each player constantly looking at other players’ moves for inspiration and learning experience. So while China and Japan are playing it out, so are India and Japan, and so are the USA and Canada and Australia and Kazakhstan and so on. While China has focused on its game, the rest of the world has been playing out its games.

The missing factor in much of this, in my opinion, has been the effect of the Global Financial Crisis caused by the housing bubble. Not because of the crisis but because of the bubble. The GFC is the most recent, most discussed, and most felt global financial fiasco of modern times. I like the historical housing prices in Figure 1 because it shows the trend lines which predict where the prices will return to once the bubble bursts and the scatter settles down. When the historical rare earth prices chart is examined and compared, it is clear that this has been a bubble too as seen in Figure 2.

![United States House Prices](https://example.com/house_prices_graph.png)

**Figure 1:** Collapse of the Housing Bubble in 2006 precipitating the Global Finance Crisis.
**Figure 2:** Comparison of housing bubble of Figure 1 and the rare earth prices of 2011 show a distinct similarity suggesting the high rare earth prices were an anomaly and not a new price level.

It is possible that some of the rare earths price hike of 2011 was caused directly or indirectly by the mentality of the GFC. Many independent commentators at the time like Jack Lifton\(^5\) and Constantine Karayannopoulus\(^6\) said as much. John Hykawy\(^7\) was prescient very early in the piece directly linking the rare earth and housing bubbles. Others like Roger Nusbaum\(^8\), Nick Kurtis\(^9\) and Mark Smith\(^10\) thought otherwise opining it was a supply and demand thing. Some built their businesses on those opinions.

**Figure 3** shows the stages of a modern global market bubble\(^11\). A bubble accelerates out of all proportion, bursts, and then settles to where the trend line would naturally come out. House prices skyrocketed, then collapsed below value, and have started to stabilize by climbing back to their normal growth curves, based naturally on capital appreciation and inflationary indices.

**Figure 3:** Stylised model of a financial or economic bubble. John-Paul Rodrigue, Department of Economics & Geography Hofstra University 2008\(^11\).
The reason that rare earths “will remain moderate and stable” is twofold. Firstly, historical prices have always been moderate. The very long term pricing chart as shown in Figure 4 shows that they came into their own as a commodity with the invention of the transistor, that there are little surges at times of technological revolution (integrated circuit, microprocessor, internet, ipods), but generally have followed what one would expect for an Elastic Market.

![Figure 4: Long term historical rare earth prices.](image1)

Secondly, prices now are probably close to or below the trend line, seen in Figure 5. There is perhaps an over compensation, so a dampened oscillation back to normal can be anticipated. That is where I think we are now.

![Figure 5: Rare Earth pricing bubble. Bloomberg.](image2)

And there is a subtle reason for the oscillation. It is based on the fundamental difference between “Supply” and “Demand”. Demand can be instantaneous: a need, a desire, an opportunity. It is a concept. Supply is a real-world effect, based on physical
and practical factors. It takes time to plan production, build factories, develop prototypes, make things. This lag causes interesting phenomena, such as the temporary spike in the first place when manufacturers have no immediate options as they search for alternatives. Afterwards the supply and demand equilibrium is shifted since once a producer finds an alternative to an expensive component, they will rarely go back, even if the price drops. A lesson for China to learn; may have in fact just learnt it.

Supply and Demand is not a snapshot, it is a process in constant flux, always struggling to maintain an equilibrium against the “noise”. Afterwards it will be easy to see what has happened, but in the midst of upheaval, all is speculation.

Bubbles are caused by a mix of avarice and sheep like blind following. What must be kept in mind is the sheer size of the world which in its modern mode is intolerant of exploitation. Giant countries forget their power in a market place is affected by the choices of billions of consumers and a couple hundred chess players.

**Rare Earth Prices Will Do Exactly This**

Since the advent of the rare earth pricing bubble, which really started to show towards the end of 2010 ending abruptly at the middle of 2011 and which has been in a spiral ever since, there has been speculation about the future prices of these critical metals.

Speculation has taken two basic forms: that which expects or hopes the prices will return to their 2011 highs and that which simply despairs about the continued decline in prices. The rare observer played it safe.

The Author’s article of June 7, 2013, “Rare Earths and Elastic Markets”, essentially dispelled the thought that prices would return to the 2011 highs arguing that those prices were an anomaly. Being a doomsayer is all well and good, but helps no one. If it is true that prices were a bubble, then what would be really helpful would be some prediction of where the prices will finally settle, at what price and when. The author is not the first to see the benefit of this.

The first problem in this exercise is to define what one actually means by “rare earth prices.” Even defining “rare earths” is complex enough let alone their prices, given that they are really a disparate group and it is dangerous to bag them together. In fact there is no such thing as a rare earth price. There are 17 rare earths, so there are 17 price trends, and each element can be supplied in several salts, blended or metal form, each with their own pricing trends. Even a so called basket price is dependent on whose basket is being discussed.
Analysis showing rare earths are an elastic markets agreed with the general opinion that at least some rare earths will return to stronger prices eventually. Which ones is another problem to solve. It is not as simple as just separating the light rare earths from the heavy rare earths which is the gut reaction. In fact there are contradictory definitions of HREE and LREE just to make it harder, and some reports refer to a middle set which is not officially recognised by the US Geological Survey. And although the HREE are generally the heavier ones from europium to lutetium they include one of the lightest; yttrium. Nothing is straight forward.

Technically the definition of a heavy rare earth, (or a light one), is based on electron configurations on an inner shell affecting its magnetic and orbital radius properties. Because of the sequence as these electrons fill out, it does follow the atomic number more or less, but it is more to do with what the chemical and physical properties are like given the unusual electron configurations. So heavy rare earths do certain things that light ones do not, such as having greater magnetic characteristics, or different crystalline structures in hard metal alloys or silicon structures. Through other cosmic forces, the odd numbered electron configurations make the heavies rarer on earth, but it is the chemical and physical characteristics of the heavies that make them important in today's technology world and their difficulty in separation (not their prevalence) that makes them expensive.

So relevant factors determining which rare earths will remain at modest prices and which ones are currently undervalued are such things as type of use (commodity or not), rarity or abundance, geopolitical importance, ease of preparation or separation, advent of new processors, changing technology, and substitutability.

The objective here is to work out if some rare earths will soar in price and if so, which ones, to what price and when. There are different ways to approach this problem, but the method chosen is based on the belief that the 2011 prices were a bubble and that bubbles tend to return to earth as an oscillation.
Figure 6: Damped Oscillation.

The mathematics of oscillation can be quite daunting, and using this model requires estimates of the level of damping. Damping is the rate at which an oscillation settles, like a pendulum coming to a stop by itself. High damping means it stops quickly and slight damping means that it takes forever to come to a complete stop. Critical damping is that unique situation where it comes to a stop smoothly, like a car halting at a stop light. It is convenient sometimes to refer to critical, half-critical and quarter-critical damping as seen in Figure 6.

It is instructive to compare the half-critical damped curve in Figure 6 with the recovery stage (return to the mean) of the generic economic bubble curve in Figure 3.

This suggests that the recovery from a bubble can be modelled approximately by a damped oscillation. The peak price eventually caves in with everyone following it, until it has over reacted and everyone brings it back, which is the reason for the reference to sheep. What can rarely be determined is the level of damping, so the prices might oscillate for a cycle or two, or if it returns to normal carefully, can be critically or even over damped.

What causes damping in a physical system is a loss of energy, a result of resistance, and there is a conceptual version of resistance happening in an economic bubble too. Oscillations and bubbles start with a push. Eventually there is resistance to the irrationality of the price when it is too high or too low, and things spring back to normal. This is a meeting of human psychology and commercial rationalisation, and is seen in the traditional supply and demand curves. This part of this research will suggest when the price will settle.

The next thing to determine is the base line, and to discover if it is linear, exponential,
increasing, decreasing, or what. This part of the exercise will suggest at what price the curve will settle and is akin to the dashed line in Figure 3.

Both of these tasks, “when” and “where”, require raw data and Metal-Pages and Gareth Hatch of Technology Metals Research, LLC have been generous enough to provide the necessary data. An example of one heavy rare earth and one light: europium and praseodymium respectively were chosen for reasons given below. Figure 7 shows the Chinese FOB prices for these over the last 5 years. The difference in price between a heavy and a light is clearly evident in this figure, which uses the same price axis on the left.

While Eu prices seem to have averaged around $US500 per ton until early 2011 when the bubble started, and then rose to above $5,500 at its peak in August 2011, they have been clawing their way back down again to $883 in June 2013 when the analysis was done and has been kept so that predictions made then can be compared to what has happened since. Although at lower prices, Pr has done the same thing, averaging something like $30 per ton before, peaking at $250 also in August 2011 and in July 2013 was at $74 per ton. Pr did seem to make a false earlier start to its bubble, starting in August 2010.

Figure 7: Monthly Rare Earth Prices.
Considering just europium (Eu) to begin with, both linear and an exponential trend lines seem to fit equally well, so both are shown in Figure 8 with no prediction as to which trend line is the closer match. Also shown at left in Figure 8 is the curve for the downward damped trend as the bubble has been bursting.
Figure 8: Rare Earth Pricing Predictions for Europium.

The reason for choosing europium is to see if non-commodity rare earth elements present a different pricing future compared with those used in commodities or consumer products. Many rare earths have uses in both markets; while europium is a toxic, reactive, rare element that has uses in a small number of applications including some that use its nuclear properties. For that reason, it is likely to have a growth market which is not strictly price sensitive, and therefore may have an exponential trend line. The oscillation curve in Figure 8 suggests that the prices have bottomed and should really be around $1,200 - $1,300 per ton today instead of the $880 it currently is. The maths (not shown) also suggests that if the growth trend is indeed exponential, the price will bounce back to a respectable $2,000 within about 8 to 12 months. If the trend is more linear, the data suggests the prices are almost back to normal, but will continue to decrease for a similar period before returning to around $1,000 per ton in less than a year. So that was the prediction for europium, that the price is undervalued and will settle at between $1,200 and $2,000 per ton in about 8 months having dropped below their value and are about to bounce back.

Figure 9: Rare Earth pricing bubble. Bloomberg.

The same exercise for Praseodymium in Figure 9 suggests that Pr prices were about right in June 2013, that the prices had returning at a ‘critically damped” rate to what
they should be if the bubble had not occurred. This means that the price of Pr at $74 per ton then has bottomed out. The trend line equation (not shown) suggests the price of Pr will double about every 4 years from now.

Praseodymium applications are concentrated in the consumer products industries, glass works, filters, flints, and so on, and as such is more likely to follow a more linear and typical supply and demand character.

Another reason for choosing these two elements is that even though they are classified as one a heavy and the other a light, they are very close together in atomic number (59 and 63). So it is the technical difference of electron configuration that is making the difference in use and price more than the physical characteristics like weight, melting point or density.

In August 2014 the price of europium is $1,000 per kglm and praseodymium is $150 per kglm (Figure 10) showing that more than a year after the original analysis and forecast made in June 2013, the prices of these two rare earths is approximately as predicted (allowing for a linear curve for europium).

![Figure 10. Current prices for europium and praseodymium (Metal-Pages) August 2014](image)

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Session IV: European Framework
EUROPEAN POLICIES ON CRITICAL RAW MATERIALS, INCLUDING REE

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Abstract
This paper deals with the criticality of REE and other materials. 'Critical' raw materials [CRM] have growing economic and technical importance, high risk of supply shortage, low political-economic stability of the main suppliers and low substitutability/recycling rates. EU policies in CRM are studied, from the 2010 EC report to current monitoring of CRM -- including the CRM list review and actions by Member States and stakeholders. Specific EU policies on mining, processing, recycling, or substitution are presented: the Raw Materials Initiative, the European Innovation Partnership on Raw Materials, taxation & trade policies, R&D in substitutes/recycling and the EU-US Free Trade Agreement. Finally, Chinese CRM policies and the WTO actions on Chinese minerals, including Mg/REE/W/Mo exports, are analyzed.

History of CRM in the EU

EC Definition of 'Critical Raw Materials'

Securing reliable and undistorted access of certain raw materials is of growing concern within the EU and across the globe. CRM have a high economic importance to the EU combined with a high risk associated with their supply1. In the framework of the Raw Materials Initiative [RMI] on which see below, the first European CRM analysis, published in 2010, identified 14 CRM from a candidate list of 41 non-energy, non-food materials2. The EC formally adopted this list in 2011 and stated that it would continue to monitor the issue and update every 3 years1. Thus, in May 2014, the EC published a revised and extended CRM list including 13 of the 14 materials from the previous list, with only tantalum moving out due to a lower supply risk. Six new materials appeared: borates, chromium, coking coal, magnesite, phosphate rock and Si metal, bringing the number up to 20 CRM. The other 14 raw materials are: Sb, Be, Co, fluorspar, Ga, Ge, In, Mg, natural graphite, Nb, platinum group metals, heavy REE, light REE and W. CRM are highlighted in the pink shaded zone in Fig. 1 below.
**Figure 1:** The 2014 Criticality Chart

EU primary supply across all candidate materials is around 9%. CRM supply from EU sources is even more limited. China is the most influential in terms of global supply. Other countries have dominant supplies of *specific* raw materials, eg the USA [Be] and Brazil [Nb]. For the platinum group metals and borates, supply is more diverse but still relatively concentrated.

**Raw Materials Initiative**

RMI aims at providing the framework conditions to establish an integrated strategy to face the challenges related to the access to non-energy and non-agricultural raw materials and tries to facilitate a sustainable supply of raw materials. Following the November ‘08 Communication that aimed at improving access to Raw Materials in Europe on a 3-pillar approach\(^3\): ensuring a level playing field in access to resources in third countries, fostering sustainable supply of raw materials from European sources and boosting resource efficiency and promoting recycling, in June 2013, the EC adopted a Report\(^4\) on the implementation of the RMI, providing an overview of the ongoing initiatives while highlighting the joint interest for the EU and third countries rich in raw materials to work in partnership. EU member states were requested to develop national strategies in support of the raw materials industry and of fostering access to resources.

**European Innovation Partnership on Raw Materials EIP**

As an RMI follow-up, the EC launched in November ‘12 the EIP to reduce the EU’s dependency on imports of raw materials; to promote production and exports both by improving supply conditions from within and outside the EU, and by providing
resource efficiency and alternatives in supply; and to bring Europe to the forefront in the raw materials sector, whilst also mitigating the sector’s negative environmental, social and health impacts, bringing together EU countries, companies, researchers and NGOs\textsuperscript{5}.

For example, new technologies can help to extract deeper, in more remote areas and under harsh conditions. Action is also needed to develop CRM substitutes and to improve recycling of, among others, the 17 kg electric and electronic equipment waste that each EU citizen produces annually today\textsuperscript{5}.

The current situation calls for targeted innovation and research efforts, breakthrough technologies and multidisciplinary approaches, as well as demand-side interventions eg standards, public procurement, regulatory measures. Such efforts are also essential for the manufacture of new and innovative products eg batteries for electric cars, photovoltaic systems and devices for wind turbines\textsuperscript{5}.

2. Other national CRM initiatives

Countries are placed in different supply chain stages. Japan is focusing heavily on substitution, China on processing and metallurgy, Australia in sustainable mining and Canada in exploration. S. Korea is investing $300m over 10 years for research into 40 technologies covering refining, smelting, processing, recycling and substitution. Russia has an active program on materials stockpiles and export restrictions. China has tightened export quotas ostensibly to secure internal supply. The US legislature has long being studying\textsuperscript{7,7a} CRM, the country had a stockpile for strategic defense materials and recently China bought a quantity of MoO for the same purpose\textsuperscript{6}.

In a broader context, concerns over conflict minerals arising from the DR Congo and neighbouring states lead to materials stewardship schemes and legislation for responsible sourcing and traceability of raw materials, eg for Co and Au the Extractive Industries Transparency Initiative and the International Council on Mining and Metals Materials Stewardship Scheme. Similarly, the US Dodd-Frank Act requires electronics companies to disclose their sources of cassiterite, wolframite and tantalum. Similar regulation is now under consideration in the EU\textsuperscript{6}.

REE Resource Efficiency and Recycling

End-of-life recycling rates for all of REE are below 1%, according a recent report by UNEP. REEs are recycled from pre-consumer scrap eg from permanent magnets. In Japan approximately 1/3 of REE for permanent magnets went into new scraps and then recycled, just like recovering the EU’s CRM, including REE, as per a recent study that identified the following recovery opportunities\textsuperscript{6}:

- Permanent magnets: hard disk drives are a current opportunity; wind turbines and hybrid/electric vehicles present a long term potential at the end of their lifetime
- NIMH batteries: from both portable electronics and hybrid/electric vehicles if they can be collected and identified. Umicore and Rhodia have now announced a jointly-developed process to recover REE concentrate that can then be refined into REE materials.
- Phosphors: Rhodia has developed a new process for the recovery and separation of REE contained in used fluorescent powder in lighting applications. identified the following recovery opportunities6:

**US: Strategic Stockpiling of CRM**

The Strategic Mineral Advisory Council is encouraging the U.S. DoD to move away from stockpiling strategic/CRM from China to creating and nurturing a U.S.-based REE supply chain7. DOD is in the process of identifying REE resources to stockpile. The Strategic Materials Advisory Council is particularly concerned about the DOD recommendation that $120.43 million of HREE, which are only produced in China, be added to U.S. stockpiles. “The root cause of these material shortages is our ongoing dependence on Chinese suppliers,” said council executive director Jeff Green. “We urge DOD to move...to the only appropriate and permanent solution—the creation and nurturing of a U.S.-based REE supply chain...[the US] must not rely on research projects and substitutions alone to close the current supply gap [and] must not accept the status quo of material and technological dependence on China. Instead, [DoD should] engage the industrial base domestically and from U.S. allies, to achieve sustainable HREE development for defense and essential civilian requirements.’ Some analysts, however, note that creating a strategic CRM could have also negative side effects eg insufficient flexibility, impact to the price of the commodity.

**3. Foreign Trade Policies on CRM**

Materials security and criticality has been of growing interest internationally. Several countries, including suppliers and users of raw materials have instigated studies and initiatives to develop national strategies for securing a stable supply of raw materials8. A number of outreach activities were pursued in international fora such as G20 and the OECD aiming at fostering a global dialogue on how to achieve a framework to ensure a sustainable supply of raw materials.

EU trade policy will continue to monitor ongoing and future negotiations of Foreign Trade Agreements and other bilateral frameworks to ensure that raw materials are considered and integrated, where appropriate. Import data on the most critical raw materials for wind energy [magnets in turbines], Nd and Dy, are collected. During negotiations for the planned Transatlantic Trade and Investment Partnership in July ‘13 the EC said that raw materials are a key priority sector to the EU and that it wants the US to ban export restrictions on selling raw materials and energy to the EU.
Industrial Minerals Trading

As well as blocking export restrictions, the Initial EU position paper\(^9\) says trans-Atlantic trade in these products could be promoted by increasing transparency and predictability of trade deals. This would be “the first and most important step towards a better [global] governance of trade in raw materials,” which, in turn, would boost investment, aid production and promoting the functioning and expansion of related infrastructure\(^10\).

Specifically, the EU wants the agreement to “encourage transparency in the process of licensing”, including the allocation license conditions for trade and investment. It wants negotiators to consider incorporating rules inspired by the global Extractive Industry Transparency Initiative [EITI] on declaring payments to governments. This Initial EU position paper\(^9\) stresses that “once exploitation is permitted [...] non-discriminatory access for resource exploitation, including for corresponding trade and investment related opportunities, should be guaranteed by regulatory commitments.”

US DoD Urges Assessment of REE Supply Risk July 11, ’14

The agency in assessing REE supply risks for the US military industry, showing the strategic importance of these minerals and the will of the US to limit its reliance on China\(^11\).

4. Chinese CRM policies

Chinese Export License Systems: REE etc

China often uses trade-restrictive measures eg export duties and quotas on key raw materials, including Sb, bauxite/alumina/aluminium, Co, coke, Cu, fluor spar, In, Pb, magnesite/magnesium carbonate, Mn, Mo, Ni, RE, Au, Sn, W, wood, yellow phosphorus and Zn\(^11\). Other discriminatory barriers for the REE processing industry include the unwritten pre-condition of any company to have their request for a permit evaluated, blocking new FDI in the sector\(^12\).

Since 2000, China applies production caps to regulate REE supply and instated an export quota system, whereby Chinese companies (including foreign JVs) have to obtain a licence to export any REE. Licences are attributed separately to domestic producers/traders and to foreign JVs. As from 2007, China collects an export duty on RE which depending on the REE varies between 15 and 25%. Since 2009, the export quotas have been reduced significantly\(^12\).

The EU is also concerned about the flexible export tax policies in the Non Ferrous Metals Stimulus Plan of 2009. The use of flexible export tax rebates clearly aims at
reducing exports of lower value products such as raw materials and this could be interpreted as a government subsidy for high-tech products with high added-value\(^\text{11}\).

**China and the CRM Value Chain**

The report “Dominating the World, China and the Rare Earth Industry” by the National Institute of Advanced Studies, Sept ‘13 \(^\text{13}\) postulates that China achieved its REE monopoly thanks to US policy oversights, including the permission to buy *Magnequench* in 1995 that allowed China to become a global player in the value chain for REM, alloys and magnets. Some members of Congress opposed the sale, pointing out that the buyers were majority controlled by the Chinese government. Through *Magnequench*, China gained access to the most important portfolio of REE patents in the world, including REE magnets for cruise missiles and other advanced military hardware. Coincidentally, ‘such components started to spread worldwide after the transfer of *Magnequench* to China’.

**Taxation**

The Chinese MIIT is considering raising taxes on REE\(^\text{14}\). A counter-argument raised by the industry is that taxes create an uneven playing field for companies operating legally, and paying the taxes, compared with illegal miners, also creating a big pricing gap between legal and illegal enterprises.

Chinese resource taxes have a history of creating unfairness, owing in part to the criteria on which they are implemented. China’s Ministry of Finance and State Ministration of Taxation raised taxes on rare earth ores in 2011, but the impact of the taxes differed greatly between provinces, due to the varying ratios of ore-to-processed REE products. In June ‘13 the MIIT sought opinions on whether to continue hiking the resource tax on REE minerals, but could not reach a conclusion, but it seems each domestic government is adopting different standards and the execution is confusing.

**REE Recycling – and Smuggling...**

*Illegal trading practices* are often used in China to circumvent direct control of important secondary raw material flows, including recycled REE. Preliminary statistics of June ‘14 show illegal smuggling hidden among 67 REE recycling projects across the country. MIIT urged the government to regulate REE recycling\(^\text{15}\).
Subsidising REE Environmental and Efficiency Upgrades

China government’s decision to subsidise REE producers pursuing technological upgrades, shows the commitment of the country to address energy-efficiency and environmental issue and to promote value-added products\textsuperscript{16}.

5. WTO

The first dispute settlement case on several industrial raw materials was initiated in June ’09 by the EU, the US and Mexico\textsuperscript{12}. No amicable solution with China was found, so a Panel was established in Dec ’09 and upheld most of the EU’s claims. China appealed certain aspects but the Appellate Body upheld all the key claims raised by the EU, and confirmed the findings made by the Panel, including [a] that China’s export restrictions on several industrial raw materials are in breach of WTO rules and are not justified for environmental protection or conservation policy reasons and [b] that China had committed not to levy export duties. For procedural reasons, the Body could not rule on additional claims regarding technical aspects of China’s administration of export quotas and licences and to a minimum export price. Preliminary analysis indicates that China has taken steps to comply with the ruling but in practical terms there are still significant barriers, eg minimum export prices seem to still be in place.

In March ’12, the US, the EU and Japan initiated a second complaint with respect to China’s restrictions on the export of various forms of REE, W and Mo used in the production of electronic goods\textsuperscript{17}. These restrictions include export duties, export quotas, minimum export price requirements, export licensing requirements and additional requirements and procedures in connection with the administration of the quantitative restrictions. A panel established with key findings that China imposes three export restrictions: export duties (taxes); export quotas on the amount of those materials that can be exported in a given period; limitations on the enterprises permitted to export the materials -- all inconsistent with China’s WTO obligations.

On 17 April 2014, China notified of its decision to appeal certain issues. At the same time, a very interesting suggestion appeared in a China Daily report: ‘Beijing should try and get around the WTO ruling by offering to remove the export quotas on LREE but keep ones on medium and HREE, which have smaller production volumes’\textsuperscript{17}.

The Ministry of Commerce says the Chinese position is really just about protecting resources\textsuperscript{18} and the environment for sustainable development. But the next sentence is something more of a stretch: ‘It has no intention of favoring domestic industry through distorted trade’.

Gao Wei, general manager of Shanghai Huaming Gona Rare Earth New Materials, welcomed the removal of the current tariff and quota systems that had weakened Chinese REE competitiveness in terms of pricing and Chinese products are priced higher than their foreign rivals because of the tariff and quota systems and said that
'Lifting the quota and reducing tariffs will help domestic producers digest their massive volumes of REE and bolster the production of medium and HREE'.

The president of the US National Mining Association, welcomed news of the WTO ruling but pointed out 'this was no panacea to solving the US's mineral supply chain woes. American companies were still 100% reliant on China for supplies of REE and other minerals [and should] develop local resources and also look downstream, in Africa, Australia, Canada and elsewhere — after all, it was a processor once upon a time and could be so again'...So far, many REE projects around the globe have secured financial backing from Chinese, S. Korean or Japanese interests. Japan is clearly aiming to end its reliance on China for REE supplies for its downstream industries. Perhaps rather than joining the long line of exploration companies looking for REE deposits, the strategy for America would be to provide the downstream money and technology'\textsuperscript{18}.

**Chinese Retaliation?**

Chinese authorities may deal with the WTO by imposing higher taxes on producers of REE on the basis of the value of minerals, rather than the volume as is the case now. This change will result in higher production and, of course, export prices. But China’s revenge could be longer-term and designed to cause deeper damage\textsuperscript{19}.

**6. What next?**

The EC report from on the Implementation of the Raw Materials Initiative’ of June 24, ‘13\textsuperscript{d} stated that ‘a wide-ranging public consultation on the strategy was going well; the majority of EU member states had responded...along with non-EU countries, regional governments and the industrial minerals industry’.

The report confirmed that by 2020 actions would include: setting up innovative pilot projects, including demonstration plants on exploration, mining and processing; finding substitutes for raw materials in short supply; creating a network of research centers on sustainable raw materials management; using EU-standardized instruments for surveying resources; creating a 3D geological map; modelling raw material trends; and undertaking complete lifecycle assessment of EU raw materials needs.

However, Roskill\textsuperscript{20} point out some disadvantages of the report, ‘hence it should be read with caution’:

- "Terms like ‘risk’ and ‘critical’ are emotive," and the end result could be panic and ‘unnecessary substitution’
- Considering “the wider supply chain dynamics” Roskill provides a case study of cobalt as CRM. Although it is right to highlight the supply risk situation in the DRC, “a volatile state does not necessarily result in volatile levels of raw material exports.” Indeed,
from 1996 to 2003, when main periods of conflict occurred, mine production increased at a 28 pct CAGR

- Metals and oil make up 95 pct of DRC’s total export revenue, with mining and quarrying accounting for ~12 pct of its GDP, hence DRC is unlikely to put policies in place that would negatively impact those industries.
- DRC is not the sole determinant of Co supply. For instance, 2/3 of Co is produced as a by-product of Ni and Cu, meaning that demand for either of those metals has the ability to impact Co supply.

On the specific issue of recycling, the following comments were made by Zboril21. Regulations on recycling have not been framed coherently and tend to focus on individual, isolated aspects of collection and recycling and do not take account of the market forces at work in the systems and processes. The conflict between market forces and the existing regulatory framework should be analyzed in detail to achieve better balanced results. The EU should possibly negotiate emergency terms with the WTO, setting clear and transparent conditions for export restrictions/duties on wastes of strategic importance. Recycling should be supported by improving collecting infrastructure, creating legal certainty and an equal level playing field and by removing unnecessary administrative burdens. Lastly, all individual elements of the EU Climate Change Policy should be the result of consistent energy, raw material and industrial policies.

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Legislation and best practice in the emerging European rare earth element industry

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Abstract

This paper explores the environmental legislation and best available technique reference documents in place in the European Union to support the emerging European rare earth element (REE) industry. One of the issues for REE mining, beneficiation and processing is the radioactivity that can be associated with the ores, arising from the presence of elevated U and/or Th and their daughter products. Therefore, workers may need to be protected from radiation during the exploitation of REE resources, and the public protected by suitable disposal of the radioactive wastes produced. Potential regulatory gaps and best practices are identified, based on the experience of countries with a REE industry.

Introduction

Rare Earth Element (REE) mining, processing and exploitation are large scale industries that use a wide range of chemical substances and generate significant quantities of waste. Additionally, the ores contain variable amounts of impurities such as non-target toxic metals, fluorine and radionuclides that may be released from the ore during processing into the product or waste streams, and/or represent safety issues to the workers. The most significant environmental impact of mining is often on the surface- and groundwater quality as seen at Bayan Obo, China¹, Mountain Pass, USA², and a processing plant in Sichuan, China³. The large volumes of tailings that are generated during hard rock mining are a source of waterborne contamination. Tailings are also a major environmental hazard if the tailings impoundment dam fails.
Dust and gaseous emissions are also important vectors for both environmental contamination and the exposure of workers to toxic substances. For example, processing at Bayan Obo has led to the release of fluoride, dust and waste gases containing HF and SO$_2$.  

Past REE mining and processing has therefore led to significant environmental impacts in several non-EU countries, including Brazil, China, Malaysia and the USA. In addition to the environmental damage caused, remediation of contaminated sites can be expensive. For example, the estimated cost of remediating the Mitsubishi REE processing site in Bukit Merah, Malaysia is $100 million. It is therefore important to ensure that the regulatory framework in the EU will support the development of a well managed REE industry with acceptably low environmental impacts. Since mining and industrial processing are established industries in the EU, there is a body of relevant legislation that could be expected to cover the REE industry. Best practice is described in best available technique reference documents (BREF) for the management of tailings and waste-rock in mining activities and the non ferrous metals industries. However, although generic environmental protection methodologies are included in these BREF, specific issues relating to REE tailings and processing are not considered specifically. Therefore, in this paper, we explore the EU legislation and guidelines that are in place to support this emerging industry and identify potential gaps.

**Naturally Occurring Radioactive Materials (NORM)**

REE ores often contain sufficient natural radioactivity to be considered naturally occurring radioactive materials (NORM). The radioactivity arises from U and/or Th and their daughter products (Figure 1) that are either co-mineralised with the REE or present in other minerals within the ore. It is therefore a safety issue at mining sites and during processing: a significant relationship has been found between the inhalation of Th-containing dusts and lung cancer in miners in a 20 year study at Bayan Obo; two REE processing plants and a waste facility in Brazil became contaminated with Th and its daughters; and workers have received elevated doses in the REE industry worldwide.

The separation of the different radionuclides in the decay chain from the REE during beneficiation and processing occurs at a point determined by the chemistry and physicochemical associations in the ore. Given that there are 8 elements within the $^{238}$U decay chain (Figure 1) and 8 in the $^{232}$Th chain, their separation during processing is not simple and it is important to ensure that the final REE products are below the NORM activity level (1 Bq/g of a single radionuclide in the decay chain). Examples of radionuclide partitioning during REE processing are given by the IAEA.
Figure 1: Radioactive decay chain of $^{238}$U ($a =$ years; $d =$ days, $h =$ hours, $m =$ minutes, $s =$ seconds)

Analysis of the Regulation of the REE Industry

In this section, EU legislation is compared with legislation in states with an existing REE industry or experience with NORM, focusing on USA and Western Australia.

Regulatory Framework

Environmental regulation and implementation of the regulations are clearly important for any potentially polluting industry, but are not without their challenges. The 11 km$^2$ tailings impoundment at Bayan Obo, China has contaminated the surrounding area$^1$, and provides an extreme example of the environmental consequences of an unregulated REE industry. Introducing regulation in China has also been difficult because of the large number of small companies and a significant level of illegal mining. Forced mergers have consolidated the industry, but the system is still reliant on a level of self-regulation. Similarly, although Russia’s legislation in many cases meets or exceeds commonly accepted international standards, its enforcement has been uneven$^9$. India has also experienced challenges trying to eliminate illegal mining, in this case due to easy access to REE-containing beach sands. Europe’s existing mining industries mean that legislation is in place and in use. The Mining Waste Directive (2006/21/EC) is a key piece of legislation, and links with the Water Framework (2000/60/EC) and Groundwater (2006/118/EC) Directives for the management of mine water. The Industrial Emissions Directive (IED; 2010/75/EU) applies to the beneficiation and processing of the REE ores, and also ties in with the Water Framework Directive and Groundwater Directive. Additionally, processing wastes are

Penalties are needed for non-compliance with the regulations and the “polluter pays” principle is embedded in legislation in the EU (Environmental Liability Directive (2004/35/EC)), in the USA (Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)) and Western Australia (Contaminated Sites Act (2003)). The Contaminated Sites Act (2003) also states the penalties associated with non-compliance, including a daily penalty to discourage delay. Environmental quality standards also support industrial regulation. In the EU, the Water Framework and Groundwater Directives require threshold values to be set for only a limited list of substances, with only some relevance to the REE industry. The threshold values set also differ between member states. In 2011, China brought in specific pollutant discharge standards for the rare earth industry

Environmental Impact Assessment (EIA)

Environmental impact assessment prior to the onset of activities is an important process for minimising the environmental risks associated with mining. The Environmental Impact Assessment Directive (2011/92/EU) applies to for EU mine sites with a surface area greater than 25 hectares. There is also a need for appropriate EIA if a proposed mine may impact a Natura 2000 site, as defined by the Habitats Directive (Directive 92/43/EEC) and Birds Directive (2009/147/EC). The definition of when an EIA is required varies between countries, but EIA is needed in the USA, Russia and Western Australia. Additionally, China is introducing an environmental risk assessment system for the REE industry.

Tailings management legislation

The tailings arising from REE mining are large-scale wastes with a significant pollution potential. The Mining Waste Directive (2006/21/EC) requires all EU waste facilities to have a permit, and the application for this includes a waste management plan for minimizing environmental impacts. Facilities with a significant accident hazard also require an emergency plan to be drawn up by the competent authority. Additionally, the operator must provide a financial guarantee before operations start to provide a resource for restoring the waste facilities. The operator must maintain the site until the competent authority approves site restoration and closure, and then the operator must maintain and monitor the site for as long as the competent authority considers necessary. This is similar to legislation in Western Australia and the USA. In the USA, wastes that are “uniquely associated” with mining and processing are excluded from being regulated as hazardous wastes (Bevill amendment), and these are instead
treated as non hazardous solid wastes. The Contaminated Sites Act (2003) in Western Australia introduces the full life-cycle costs principle, which ensures that the cost of effective waste disposal is included in the cost of the products. Western Australia also has specific guidelines on safe design and operating standards for tailings storage\(^{11}\), which play a similar role to the BREF for the management of tailings and waste rock in mining activities in the EU\(^4\). However, Western Australia also provides specific guidelines for the handling of the NORM mining waste\(^{12}\), which is not the case in the EU.

**NORM legislation**

The explicit inclusion of NORM in the latest versions of the IAEA Basic Safety Standards (2011) and the EU Basic Safety Standards (2013/59/EURATOM) will support more consistent regulation of NORM. However, the actual regulation of the handling and disposal of NORM wastes differ between countries and EU member states. The EU Basic Safety Standards state that “activities in industries processing materials with naturally occurring radionuclides, or activities related to such processing” are within its scope, suggesting that REE mining and processing are relevant. This is already the case in the UK, where REE mining and processing are specifically identified as a NORM industry that falls under their national regulations. The new BSS also address worker exposure to radon explicitly, which will be important for both worker exposure and waste management in the REE industry.

Countries with large scale NORM industries have developed their regulations of NORM wastes to a higher level than others, often taking lead from the UN, ICRP and IAEA. Norway has integrated its legislation for activities that involve or may involve radioactive pollution or radioactive waste management into its 2011 Pollution Control Act, which controls their permit system\(^{13}\). A repository has also been built for the disposal of NORM wastes from the oil industry with > 10 Bq g\(^{-1}\) of \(^{226}\)Ra, \(^{228}\)Ra or \(^{210}\)Po. The repository is operated by a private company, and the owners are required to have a fund for closure and remediation. The state has also guaranteed to manage the site if the company is no longer able.

In Australia, radioactivity is regulated by the Radiation Protection and Control (Ionising Radiation) Regulations (2000). However, since these regulations define ‘radioactive ores’ as those with a specific activity greater than 35 Bq g\(^{-1}\), the mining, processing and waste disposal of lower activity ores are regulated through state-level environmental and mining laws. The Australian Radiation Protection and Nuclear Safety Agency (ARPANSA) provides The Code of Practice and Safety Guide: Radiation Protection and Radioactive Waste Management in Mining and Minerals Processing\(^{14}\) to support the legislation, and this gives prescriptive practice-specific radiation safety requirements. Additionally, Western Australia has extensive guidelines for managing NORM in the
mining and processing industry\textsuperscript{12}. A Radiation Management Plan and a Radioactive Waste Management Plan must be written and approved prior to any work taking place that involves NORM\textsuperscript{14}. The depth and level of detail of the Radioactive Waste Management Plan should reflect the amount and activity of the wastes, as well as the degree of processing, as this can affect the ease with which radionuclides leach. The dilution of NORM tailings (prior to any chemical treatment that breaks secular equilibrium) with lower activity waste from the same site is encouraged to reduce the overall activity concentration to below the regulatory limit. Dilution is also allowed for materials to be used in other activities such as road building\textsuperscript{12}. Potentially valuable tailings can be stored in tailings dams if adequate safeguards are in place\textsuperscript{12}.

**Management of the mine site**

As well as requiring management during operation, mines also require stabilisation and monitoring during idle periods, which typically occur when the market price of the commodity falls, and long term post closure management. Failure to stabilise sites effectively can lead to unauthorised discharges, as seen at the Pea Ridge mine and the South Maybe Canyon mine site, USA\textsuperscript{2}, both of which have REE-rich ores. The EU does not have direct legislation for mining, but uses a variety of legislation including the Mining Waste Directive (2006/21/EC) discussed above. This influences mining permits since tailings are often disposed of at the mine site. It is strengthened by Seveso III (96/82/EC), which addresses operator responsibility to prevent major accidents, with disused mines as well as disused and operational tailings disposal facilities being within the scope of the directive. However, given the legislative approach in the EU, aspects of mine management are not addressed explicitly and, as a result, there are differences between the regulations in different member states. A different legislative approach in the USA (Surface Mining and Control Act of 1977) gives more direct control of the mine, including idle periods and post closure. The waste rock piles, the tailings ponds, and other mine areas must be stabilized and managed during idle periods, and restored to its previous condition on closure.

Site management in the case of bankruptcy is another important issue, given the large sums of money involved in waste management and site remediation. The USA has a “superfund” (legislated in CERCLA) generated by a tax on chemical and oil companies, which can pay for the Environmental Protection Agency to clean up hazardous abandoned sites and respond to short term emergencies. In Western Australia, the Director of an insolvent company may be liable for the costs of remediation if the insolvency is linked to avoidance of responsibility for site remediation. Ultimately, if the director is also bankrupt or not judged to be liable, the state takes responsibility.

There is currently a discussion of a disaster risk-sharing fund in the EU to cover large scale industrial accidents (damage exceeding €100 million), funded by a mandatory
insurance premium of a percentage of the annual net sales. A report prepared for the EC\textsuperscript{15} raises questions relating to this. The fund could not subsidise operators or it would be in breach of the polluter pays principle, but if the funds are to be re-paid, there is the question of whether liability should be capped. Different industries have different levels of risk and there are differences in the extent to which environmental damage is covered by existing private insurance in different member states.

The Non-Extractive Industry Panel suggests that the fund is unnecessary in the EU, given the stringency of the Environmental Impact Assessment, Mining Waste, Seveso III, and Environmental Liability Directives, and the financial controls they define\textsuperscript{16}. They argue that adherence to the EU law should make the fund unnecessary, and that the fund may encourage low standards in industry. However, environmental protection against large scale accidents does need consideration, as does the management of sites and contaminated land that are no longer under ownership. One issue here is licensing of subsidiaries, whose financial losses are not covered by the parent company. Equally, the financial guarantees associated with the Mining Waste Directive may only cover a relatively small part of the overall costs.

**Conclusions**

The regulations to support REE mining and processing industries in Europe generally compare favourably with international standards. The main issues that have been identified here are:

- several different pieces of environmental legislation control aspects of REE exploitation in the EU, which emphasizes the need for focused guidance documents
- the next updates of the relevant BREF documents\textsuperscript{4,5} should therefore include REE-specific information, including the management of NORM
- the current environmental quality standards should be reviewed to encompass the main hazards associated with REE mining and processing
- there is a lack of direct legislation for mine management, which may lead to differences between the regulations in different member states
- REE NORM waste management regulation is likely to differ between member states
- the question of funding for remediation of abandoned sites is relevant to REE mining

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A COMPARATIVE ANALYSIS OF NATIONAL RAW MATERIALS POLICY APPROACHES - WITH A FOCUS ON RARE EARTH ELEMENTS IN EUROPE

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Abstract

The EU is highly dependent on raw material imports due to a combination of factors, such as price volatility, geo-political regimes affecting trade, and a global surge in demand. Consequently, in 2008 the European Commission launched a process for the development of a policy framework (1, 2) fostering the sustainable supply and use of raw materials. However, since many regulatory issues are in the competence of EU Member States, specific and tailor-made policy responses need to be designed and implemented on the national level.

Therefore, this paper analyses national policy mechanisms in 4 EU Member States (Austria, Finland, Greece, and Sweden) that address REE challenges and formulate policy responses in the context of general raw materials policy. It will shed light on policy instruments and governance procedures regarding different approaches to tackle raw materials supply in the context of governance for SD (participation, reflexivity, and long-term vision and short term action). Hence, the paper’s remit lies in explicating the policy governance regime and making a case for best practices with regard to different sustainable raw materials supply approaches.

Introduction

Overall, the functioning of economies and society’s well-being largely depends on the secure supply and use of natural resources and raw materials in particular. However, with world population projections estimating more than 9 billion in 2050 and rapid economic growth in newly industrialising countries, raw materials demand continues to rise strongly (3, 4). Furthermore, per capita raw material consumption is currently substantially higher in industrialised nations than in less developed countries (5).

Continuing population growth, combined with increasing affluence, does not only put a strain on resource availability, but also influences the amount of waste and emissions produced. In the long run, these trends will lead to surpassing planetary boundaries and thus will also affect the well-being of people and the environment (6, 7, 8).
Additionally, the rapid development of emerging economies in the Asia-Pacific region led to an increased metal ores and industrial minerals consumption by a factor of 8.6 during the period of 1970-2008 (9). Furthermore, if the world economy continues to grow following its current development path, i.e. a “business-as-usual” scenario, global resource extraction would significantly grow in the future (10).

**European Union security of supply challenges**

Threats to secure supply of certain raw materials and the emergence of critical materials in the EU depend on a series of different political, economic and technological factors. Among the most crucial factors threatening EU’s secure supply of certain raw materials is its high dependency on raw material imports. In 2011, for example, the EU trade balance (5) for fuel and mining products showed an immense asymmetry between imports and exports (i.e. the EU imported over six times more fuel and mining materials than it exported).

In this regard, the EU’s import dependency is subject to a range of market distortion factors, such as price volatility, as well as the interaction (i.e. distortions through in-transparency and speculation) between physical and financial commodities markets, and export restrictions or privileged access (2). Beyond international aspects, competition on different land use types (recreation, agriculture, built-up land) might further restrict the access to European raw material sources (11).

In addition, the physical raw material demand for development and rapid diffusion of key enabling technologies such as renewable energy technologies in the future will aggravate these trends (11, 12).

**The European Union raw materials policy framework**

Besides tackling environmental and social impacts of raw material supply and use, one of the major challenges in the raw materials policy debate is to achieve a secure supply base. Raw material shortages are an imminent threat to the EU’s secure supply and availability.

As a consequence of these above mentioned trends, the EU acknowledged the importance of raw materials supply for its economic development and society overall. Thus, in 2008 the EU instigated the Raw Materials Initiative (RMI) to manage responses to non-energy and non-agricultural raw material issues. As outlined by Tiess (13), so far the European Union did not pursue a common minerals policy.

Since then, the EU has pursued a 3 pillar-based approach to improving access to raw materials for Europe (see Figure 1) which got reinforced in a new strategy document in 2011 (2). This three-pillar approach encompasses actions on “1. ensuring a level playing field in access to resources in third countries”; “2. fostering sustainable supply of raw materials from European sources; and “3. boosting resource efficiency and promoting recycling.” (1). Another important element of this strategy engages in an international approach by embedding the EU raw materials policy agenda in the wider
set of its external policies. In this regard, it aims to foster good governance, human rights, conflict resolution, transparency of activities, and creation of local value added in developing countries.

Furthermore, recent developments dealing with security of supply issues in EU policy directly (European Innovation Partnership-EIP) or indirectly (i.e. through resource efficiency and waste management policies: Europe 2020 "Resource Efficiency Flagship Initiatives"; "Roadmap to a Resource-Efficient Europe") have been put forward. Since then, these strategies are shaping the European policy framework on raw materials security of supply and resource efficiency.

Subsequently, this EU level development triggered the design of several raw material or mineral strategies (henceforth referred to as National Raw Material Strategies – NRMS) in several EU Member States (Austria, Denmark, Finland, France, Germany, Greece, the Netherlands, Portugal, Sweden, United Kingdom) to better accommodate particular national economies raw materials needs and specific circumstances.

A Rationale for a governance for SD approach in raw materials strategies

In that sense, this paper investigates how the European framework for sustainable supply and use of raw materials outlined in the Raw Materials Initiative (RMI) and the role of rare earth elements (REE) scarcity is taken up in tailor-made policy strategies at the national level in four European Member States (Greece, Finland, Sweden, Austria).

From our perspective, we detect three specific aspects why governance for sustainable development (SD) plays a major role for successful NRMS:

1. The RMI calls for “defining a National Minerals Policy, to ensure that mineral resources are exploited in an economically viable way, harmonised with other national policies, based on sustainable development principles (...)” (12). Following this proposition for SD within National Minerals Policies, we argue that governance principles for SD (14) are a fundamental basis for applying effective minerals policy at the national level.

2. Overall, governance for SD consists of major building blocks, such as stakeholder participation and reflexivity that are prerequisites for societal self-steering. Specifically, with regard to the inclusion of non-state actors in policy making and societal steering in general, governance for SD provides a striking rationale: In that sense, governments usually have certain limitation, for instance, lack of necessary authority or means to tackle societal challenges, and difficulties to achieve general legitimacy or support from interest groups (15). Following these limitations, governance for SD refers to the involvement of and interaction among multiple societal actors for a deliberative process of collecting and generating knowledge to successfully tackle societal challenges (14). In the context of sustainable raw materials management, and, in particular, the extractive sector multi-actor approaches (16) guarantee greater commitment and acceptance for state-designed intervention (EIP on Raw Materials).
3. In the context of primary extraction and, particularly, challenges tackled in NRMS, a large number of diverse stakeholders are directly impacted or involved, and a manifold set of issues are to be addressed. Such stakeholders and issues cover, inter alia, “not in my backyard” constellations and local communities, mining impacts on ecosystems, long-term business investment decisions for prospection and extraction etc. Consequently, governance for SD aspects, such as inclusive stakeholder participation during NRMS design and implementation, are crucial to facilitate legitimacy of policy options and steering.

Following this rationale, we will shed light on policy instruments and governance procedures during the design and implementation phase with regard to governance for SD principles: participation, reflexivity, and long-term vision as well as short term action. Thus, the paper’s remit lies in explicating different approaches to tackle raw materials supply in the context of governance for SD.

Methodology

The data basis for the analysis was created by a two-pronged approach: Through desktop research of the respective policy documents (i.e. NRMS of Austria, Finland, Sweden and Greece) and qualitative interviews with policy makers of the respective countries (who carrying major responsibilities for design and implementation of corresponding strategies) form the basis of the data collection methodology. The four strategies in our analysis are:


By means of these two data collection methods, the authors address the following research questions:

Firstly, the questions to what extent major building blocks or governance principles for SD are incorporated into the strategy by means of qualitative interviews with policy makers. In doing so, the authors apply as analytical criteria for principles of governance three major buildings blocks to the concept of governance for sustainable development: i) participation and stakeholder involvement, ii) reflexivity and learning, and iii) long-term visioning and short-term action.

Secondly, the authors investigated the specific role rare earth elements play with regard to the three-pillar approach by means of text analysis and interviews with policy makers.

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1 Ministries of interviewed policy makers: Federal Ministry of Science, Research and Economy (AT); Ministry of Employment and the Economy (FI); Ministry of Environment, Energy and Climate Change (GR); Ministry of Enterprise, Energy and Communications (SE)
Results

The following paragraphs explicate on the research questions outlined in the methodology section: In doing so, the first part outlines the policy genealogy and how specific EU Member State conditions are taken into account, and the role of access to REE plays. In the second part the authors outlined the degree to which governance principles for SD (i.e. participation, reflexivity, and long-term visioning and short-term action) are applied during the design and implementation stage of NRMS.

Policy genealogy and driving forces of national raw material strategies

As regards the four represented case study countries, all share the fact that their present NRMS is the first umbrella strategy encompassing a strategic approach towards access to raw materials on a national level. Greece, Sweden and Finland reported that the EU level policy framework – the 2008 RMI – was the common driver for initiating the development of their NRMS. Only in the case of Austria, in 2001 the parliament (“Nationalrat”) instigated the development for an overall strategy for more cross-cutting as well as coherent policy mechanisms securing access to raw materials. In that sense, the Austrian Mineral Resources Plan, although still influenced by the RMI, has been considered as a best practice example by the European Commission.

Apart from the European Commission providing a major impetus for the development of NRMS, national framework conditions have strongly contributed to their development and content focus. In particular in the case of Sweden and Finland, economic factors played a major role. In these two countries, a “mining boom” through increased investment in mining and exploration activities led to augmented political awareness on the extractive sector's activities. Moreover, environmental challenges and more effective land use planning (avoiding conflicts in use and guaranteeing access to important mineral deposits) have been vital concerns for the development of the Austrian and Greek strategies. In Austria, the issue of public acceptance or conflicts with local communities for on-going and future mining projects contributed to development of a NRMS.

Prior to this development, none of the four countries did have a coherent and strategic approach (i.e. predecessor umbrella strategy) for access to raw materials from domestic sources. Instead, these countries only had a mix of single stand-alone instruments addressing different issues, such as land-use planning, covering different materials and different industrial sectors. Only in the case of Greece, mineral policy has been managed through a tripartite approach of three different laws for raw materials forming a more coherent framework.

Addressing access to Rare earth elements

This paper explores to what extent NRMS are focusing on access to REE and if they foresee concrete actions. As regards the four country cases, none of the strategies
makes a clear reference or encompasses actions specifically addressing access to REE. Nevertheless, in some countries, non-commodity specific actions include aspects on REE scarcity and access. In relation to exploration activities Greece and Austria either already identified respective deposits (Austria) or are currently prospecting for potential deposits or anomalies (Greece). Sweden is taking measures for a criticality assessment of certain materials where REE might play a role. Interestingly, in Finland some companies involved in the implementation of concrete strategy actions consider extracting REE from old tailings in case world market prices increase.

Despite some more sporadic and unspecific efforts with regard to REE, none of these countries engage in actions for REE extraction yet. However, increased efforts for exploration (Greece) and safeguarding access to deposits by restricting other land uses (Austria) might lead to future extraction projects.

While there is no significant REE production in Europe, but only uncharacterised and unexplored deposits (21), NRMS of Austria, Finland, Sweden and Greece show no commodity specific focus on securing REE supply. This to some extent depicts a perceived mismatch of EU level topical importance of REE supply compared to EU MS follow up in NRMS. Nonetheless, the RMI’s other two pillars cover issues such as raw materials diplomacy with exporting countries and strategies increasing recycling rates of WEEE which highlights a different non-primary extraction approach towards securing REE supply. These two pillars are taken up in several EU MS policy strategies but go beyond the scope of this paper.

**Participation and stakeholder involvement in policy design and implementation**

One of the key principles of SD is participation and stakeholder involvement throughout the whole policy cycle (i.e. ranging from policy design to implementation, evaluation and revision). In that sense, we asked policy makers about the respective role stakeholders (state as well as non-state actors) played in the design, implementation and monitoring of the respective NRMS.

In general, depending on the responsibility for raw materials management in the respective country, the ministry of environment (Greece) or the ministry of economics (Austria, Finland, Sweden) had the main responsibility for policy design.

In terms of involvement of state actors, the four countries cases basically feature three different collaboration approaches during the design phase of NRMS: 1) exclusive development, 2) partially inclusive, and 3) fully inclusive strategy development process. The three approaches are based on the degree of involvement of i) state actors (i.e. ministries), and ii) non-state actors (i.e. industry, public authorities, academic as well as private research institutions, and civil society organisations such as environmental NGOs).

Concerning the exclusive development approach, the Greek Ministry of environment was solely responsible for strategy development, involving only a limited number of
non-state actors, such as one industry association, one public authority and two academic institutions. On the other end of the scale, the Swedish NRMS is characterised by a fully inclusive development approach: Not only have all ministries been consulted and involved in the design process, but also a broad variety of non-state actors covering industry, public authorities, academic and private research as well as civil society and environmental organisations. Both Austria and Finland are characterised by a partially inclusive development process, involving two ministries in the co-development process and a number of non-state actors such as industry, public authorities, academia and private research as well as civil society and environmental organisations.

In a next step, we explored the extent to which non-state actors are taken on board during the *implementation* of actions of the respective NRMS. For our four country cases, we again identified three different approaches for strategy implementation and the role non-state actors play: 1) "state-actor-only implementation", 2) "shared but differentiated implementation", and 3) “fire-and-forget implementation". As regards "state-actor-only implementation", the Greek NRMS is mainly followed up by state actors (i.e. ministry of environment supported by other ministries where responsibilities overlap). Non-state actors are involved on a rather ad-hoc and on-demand basis in respective consultation procedures or committees during the implementation process. A similar case can be found concerning the steering of the Austrian NRMS where the responsibility for implementation is not located on national ministerial level but rather on the level of federal states.

An implementation approach with a higher degree of non-state actor involvement ("shared but differentiated implementation") is applied in the NRMS of Sweden. Essentially, the government appoints one authority responsible for implementation of individual actions. More specifically, the government provides the framework conditions (financing, goals and targets, time-frames, monitoring), whereas these authorities enjoy a considerable amount of freedom and independence during the implementation process.

Concerning the more active role of non-state actors, Finland’s NRMS allows for the largest degree of freedom and non-state actor involvement during implementation. Generally, the responsibility for implementing action proposals (outlined in the 2013 action plan) in the NRMS is split among different actors: State-actor steering is limited in so far, as the action plan only comprises non-binding advice on actor’s involvement and provides opportunities for new actors entering action proposals. Leading actors in these actions proposals cover a broad variety, such as industry associations or environmental NGOs. These actors are also participating in the government steering group which regularly follows up on the development status of strategy implementation.

Finland and Sweden, when compared to Austria and Greece, feature greater inclusive stakeholder participation during NRMS action implementation and to a lesser extent
in policy design. Since primary extraction challenges necessitate such multi-stakeholder approaches (see for example recent EU policy developments such as the EIP on raw materials), these policy regimes, on the one hand, might contribute to increased legitimacy for steering, and, on the other hand, facilitate implementation of individual actions.

**Reflexivity and learning in the implementation process**

Another important building block of governance for SD refers to the concept of reflexivity and learning as an ability to adapt to changing conditions within a given (governance) system. The following paragraphs highlight the instruments for monitoring and evaluation applied in NRMS to adapt to either changing framework conditions or respond to varying degrees of action implementation.

Generally, the four country cases exhibit quite diverse systems, e.g. applying more ad-hoc or systemic and ex-ante in-built approaches towards institutionalised learning in NRMS.

Regarding Greece, for example, 9 broad objectives are outlined in the NRMS for which currently no monitoring or evaluation mechanism (i.e. no indicator or assessment frameworks) exists for assessing the implementation status. In the case of Austria, the main criteria for successful implementation will be the translation of the major instrument (land use planning law) into federal state law. However, no current monitoring and evaluation system exists to measure its implementation process.

The Swedish NRMS applies a mixed approach of several targets apportioned to 12 actions areas and two horizontal objectives. However, no concrete indicator framework exists for measuring these targets but instead the responsible authorities produce a yearly qualitative evaluation report. This report not only informs the government and all involved actors but also a wider group of stakeholders at a yearly forum.

On the other end of the scale, Finland developed the most comprehensive system for policy learning and reflexivity. Besides a set of 12 general as well as specific objectives, the NRMS features an indicator framework for following up on the measurement of objectives and produces a qualitative evaluation report.

As regards reflexive learning, concrete evaluation and monitoring approaches combined with multi-actor involvement, as in the case of Finland and to a lesser extent for Sweden, allows for flexibility to address changing conditions and facilitated by the collective knowledge and understand of plurality of interests and needs.

**Engaging in long term visioning and short term actions**

This part engages in the process of envisioning long-term transformation processes, fundamental to sustainable development, and translating them into short term actions necessary for applying policy instruments.
Generally, the patterns of specific time frames, actions, and overall implementation frameworks is quite diverse: While Greece, Austria, and Sweden do not have a concrete implementation or roadmap, Finland has a fully fledge “sustainable extractive industry” action plan. In order to better understand the different nature of implementation framework, we categorised the four country cases into 1) no implementation framework (Greece, Austria) with “continuous and unspecific”, 2) “overall specific”, and 3) “differentiated specific” time-frames and actions for implementation.

With regard to the first category, we consider a continuous implementation of actions (no concrete action plan or implementation framework) with no concrete time schedule for specific actions. While in the case of Greece, a mix of short and long—term actions are initiated and followed up in a step by step basis, the Austrian NRMS' major instrument is under gradual negotiation with federals states for changing their legislation accordingly.

Furthermore, “overall specific” in the case of Sweden refers to a partial implementation framework which considers an overall time frame (3 years) for short as well as longer-term actions with a specific financial framework for that given period. On the other hand, Finland developed a fully-fledged policy action plan (2013) encompassing differentiated and specific implementation time frames across short and longer term actions.

Considering, on the one hand, for long-term perspectives while, at the same time, strategically designing implementation for the short-term, is especially relevant for successful societal transformation processes, such as sustainable development in the extractive sector. In that case, Finland provides a best practice case through a balanced combination of:

- Long-term envisioning: such as a set of broad objectives outlined in an umbrella strategy (i.e. NRMS), and at the same time; and
- Short-term actions: strategically designing short actions accompanied by specific time-frames, implementation pathways, financial framework and multi-actor consortia (i.e. policy action plan).
Discussion and conclusions

As outlined in the previous sections, EU MS NRMS demonstrate diverse policy regimes with regard to 1) the three major building blocks in governance for SD, and 2) the actual accentuation for securing REE from a primary extraction perspective.

In a nutshell, we want to highlight four major differences and similarities in terms of approaches to REE supply and policy governance regimes for SD:

- Common among the four selected NRMS is a perceived mismatch of EU level topical importance of REE supply compared to EU Member State follow up in NRMS in the area of primary extraction.
- Since primary extraction challenges necessitate multi-actor approaches, Finland and, to a minor extent, Sweden support these policy regimes and, thus, contributing to increased legitimacy for steering and facilitate implementation of individual actions.
- Concrete policy learning approaches, combined with multi-actor involvement as in the case of Finland and to a lesser extent for Sweden, allow for flexibility to address changing conditions facilitated by collective knowledge.
- Both, considering long-term perspectives and, at the same time, strategically designing implementation for the short-term through policy roadmaps and action plans (Finland), is especially relevant for successful societal transformation processes such as sustainable development in the extractive sector.

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Assessments of boundary conditions and requirements for Rare Earth Underground Mining due to presence of NORMs

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Abstract
Rare earths contain NORMs, such as uranium, thorium and their progeny, like radium and radon. The varying concentrations of NORMs are quite often significant enough to result in occupational and environmental radiation exposures during the mining, milling and processing procedures of rare earths and compounds. Ventilation is the primary technique of controlling ambient concentrations of radon. Fresh air volume flow rates, the distribution of airflow within the mine and the radon emanation rate are primary factors affecting such concentrations. In this paper, it is attempted to determine the factors that may result in radiation risks and evaluate the boundary conditions that will contribute to the restriction or even elimination of radon progeny, with a goal to use the evaluations in order to build an overall assessment tool.

Presence of NORMs in Rare Earth Elements
Rare Earth Elements (REEs) in economically exploitable concentrations are mostly found in minerals such as bastnaesite, monazite, xenotime, gadolinite, fergusonite, samarskite and allanite. All of these ore minerals contain low to significant levels of thorium and uranium series nuclides. They are thus typical examples of the Natural Occurring Radioactive Materials (NORMs). Rare earths themselves contain naturally radioactive isotopes as well, such as 138La, 142Ce, 144Nd, 145Nd, 147Sm, 148Sm, 149Sm, 152Gd, 156Dy and 176Lu. The uranium content within rare earth minerals varies from insignificant percentage to 0.8 wt. % while the thorium content varies from 0.1 to 10 wt. % depending on the mineral and occurrence. Bastnaesite (Ce, La)CO₃F contains 0.1–0.2 wt. % thorium (ThO₂) and negligible concentrations of uranium (U₃O₈). Monazite (Ce,La,Pr,Nd,Th,Y)PO₄ contains 0.2–0.4 wt. % U₃O₈ and 4.5–9.5 wt. % ThO₂. Xenotime Y(PO₄) contains almost equal percentages of uranium and thorium, 0.81 wt. % U₃O₈ and 0.83 wt. % ThO₂ respectively¹.
Radioactive Decay Chains of NORMs

NORMs decay with respect to time into many elements called ‘daughters’, a process associated with the release of radiation. The list of subsequent daughter products is known as the ‘decay chain’. Radon is a product of the radioactive decay chain of primordial uranium or thorium (Fig. 1), specifically the isotopes $^{238}$U, $^{235}$U and $^{232}$Th. The isotopes formed from this decay are, $^{219}$Rn (‘actinon’), $^{220}$Rn (‘thoron’) and $^{222}$Rn (‘radon’). Due to the low abundance of $^{235}$U and the short half-lives of thoron (55.6 sec) and actinon (3.96 sec), most work concentrates on $^{222}$Rn and its progeny.

![Decay Chain Diagram]

Figure 1: Uranium decay chain with the half-life of progeny (Source: SSVEE).

Radon is unique among the decay products because it is a gas, thus is capable of migrating from the source location into the atmosphere. It is colorless, odorless, tasteless and chemically inert with a half-life of 3.82 days. Radon undergoes 4 rapid decays, forming airborne progeny, starting with $^{218}$Po (‘polonium’) which decays into $^{214}$Pb (‘lead’), which decays into $^{214}$Bi (‘bismuth’) and finally into $^{214}$Po (‘polonium’). On entering the mine atmosphere and without sufficient ventilation, this decay chain leads to significant radioactivity (alpha, beta and gamma radiation) in the mine.

Occupational Exposure Limits and Impacts on Human Health

Radon concentration is measured in units of radioactivity rather than mass because the actual mass involved is too small. Common units are; the Becquerel (Bq) for radioactivity and the Sievert (Sv) for the equivalent dose in the human body, while sometimes in mining the historic unit Working Level (WL) is also used. Occupational exposure limits were derived to protect...
the health of underground miners over a working lifetime. The recommendations issued by
the International Commission on Radiological Protection (ICRP), are that no person shall be
exposed to more than 14 mJh/m³ (≈4 WLMs) annually. The effective dose is 20 mSv/year
averaged over 5 consecutive years or 50 mSv allowed in any 1 year⁵. The lifetime limit is 400
mSv.

Occupational exposure of underground miners to radon has been related to severe health
impacts decades ago, making it the second leading cause of lung cancer after cigarette
smoking⁶. It was first identified as a cause of cancer in uranium miners in 1924⁷. But despite
the fact that most studies are focused on its bearing risks, it is not the radon itself that is
actually responsible for the health problems, but rather the short lived radon daughters
(SLRDs) and their decay products, as described above. The radon may be thought of merely a
source for the SLRDs.

Factors Resulting in Radon Spreading in Underground Mining

Radon and progeny emanation can be attributed to their natural occurrence inside the rare
earth element bearing minerals. However, the emission of radon from the undisturbed rock
can be considered as insignificant compared to the amount of radon released after the
rupture of the ore during mining, when the specific surface area of the rock increases. It’s
spreading in the mine atmosphere, combined with the failure to restrict and/or eliminate it,
may be imputed to a series of factors.

It is of utmost importance to evaluate boundary conditions such as dust reduction, the
residence time of the excavated ore in the mine sites, the possible bioleaching of the ore, the
haulage system, the operation of crushing and grinding mills, as well as the use of tailings in
potential backfill mining. Moreover, one of the most important factors responsible for radon
concentration is the lack of sufficient air flow in the mine. Inadequate ventilation may result
in the insufficiently slow removal of radon gas, thus giving it time to accumulate inside the
mine atmosphere (Fig. 2). Another factor is the presence of groundwater in a REE mine. Radon
partially dissolves in water and thus can be transported further away by groundwater flow.
Water-borne radon will inevitably be outgassed into the air due to de-pressurization and
constant agitation⁸. Much of the radon will also decay before it has the opportunity of release.

Assessments for Controlling Radon and Progeny Emanation

The evaluations for maintaining a safe working environment in rare earth mines are basically
the same as in conventional mines; however, the occurrence of significant amounts of
NORMs, that are the focus of the mining operation, imposes special boundary conditions in
order to prevent them from having sufficient time to build up
Figure 2: Ascending of radon and radon daughters’ concentration versus time after drop down of ventilation (Reinhard Wesely, 1983).

significant quantities of their progeny. These conditions can be established based on those applied to uranium mining operations. However, it needs to be stressed that, different to uranium ore deposits, REE deposits will have, in many cases, a Th rather than a U tenor.

Mine planning

Ore dust presents the dominant source of exposure to radon and progeny, thus a proper mining method selection can reduce the dust production. As in every case, there is no single appropriate mining method that will efficiently deal with all the radiation issues and risks. Excavation techniques, crushing and transportation as well as the long time residence of the broken ore in the mine should be the operations to evaluate so as to keep radon accumulation below the occupational safety standards.

Common excavation practices can be separated into mechanical excavation and use of explosives. With respect to dust production during mechanical excavation, several studies have been made, indicating that the deeper the cut and the larger the chips, the less dust is produced from the ore removed\(^7\). The sharpness of the cutting tools is also a factor, since worn bits without their carbide tips produce much more dust\(^8\). When it comes to drilling, dust can be controlled with dry collectors at the tip of the drill bit or with water injection through the drill steel. Foam injection can also be used when excessive water is a problem\(^9\). Blasting is done when no one is expected to enter the affected area. Consequently, blasting should take place at the end of the shift when all other operations are finished.

During dropping and transporting of the mined ore, dust can also be produced in significant amounts. Depending on the mining method, the broken ore may fall from several meters height to the ground or can travel long distances through conveyor belts, that can be of
moderate cost but may be a significant source of dust, or mine railways that usually generate less dust. Enclosure, drenching and ventilation are the primary techniques to deal with these dust emission factors. In the case of wetting the ore on conveyor belts, the amount of water is an issue again for not leaving a sticky mud residue on the belts. Radon-bearing ore dust can be accumulated in areas where crushers and mill plants are installed. In REE mining it would be preferable not to have a crushing plant within the underground mine, yet if inevitable, strict dust control measures should be implemented.

Adequate wetting can be extremely important for dust control. The majority of the dust particles are not released to the air, but stay attached to the surface of the broken ore\textsuperscript{10}. The presence of water, though, may be an additional problem and the ample drenching of the ore within the limits of necessity is crucial. Furthermore, remote operation of machinery or cabins in all vehicles for the machine operators, either during mining or mucking of the ore should be evaluated as a condition that reduces human exposure to radioactivity. Personal protection devices such as dust masks can be used. Job rotation is also recommended in high concentration areas.

Some mining methods raise more issues than others. Bioleaching is a cost effective method, but most of the excavated ore is left underground creating high radon levels that are difficult to control. Similarly in shrinkage stoping, the residence of the ore on site will result in radon and progeny accumulation. Among REE mines applying cut and fill methods, those using tailings as backfill are found to have higher radon levels than those using rocks or cement. Concrete can be used to reduce radiation from the exposed ore on the back or walls; therefore it could also be used as part of the backfill mixture. In sublevel stoping the broken ore is falling from significant height, creating the “piston effect” that leads to generation of big amounts of ore dust. The sublevel caving method is well suited for a high degree of automation and remote operations with corresponding high productivity; however this method may result to high radon progeny concentration levels and should thus possibly be avoided.

**Ventilation**

The design of the overall ventilation system in a REE mine is based on the mining operation; on ventilation-air-transit time; on radon emissions from the wall-rock and broken ore, the haulage, the tailings backfill and the groundwater. The aim is to lower radon residence times to 10-15 minutes, in order to attain a limit of 10-20\% of the theoretical yield of progeny in the atmosphere\textsuperscript{11}. It is the total air volume flow rate through the mine that determines the time air takes to travel from the inlet to the production areas and to the outlet of the mine. The primary applications are main fan and multi-fan ventilation systems. Main ventilation can either be forced (blowing), exhaust (suction) or a combination of the two. Multi-fan ventilation uses forced, exhaust, main and auxiliary fans, and a parallel multiple fan operation technique based on energy saving and building partition ventilation\textsuperscript{12}.
With respect to radon confinement, forced ventilation is more effective, even mandatory in many cases and countries. In forced ventilation the positive pressure on the intake airway not only prohibits radon from being released from rocks but also blocks it from entering into airways that channel fresh air into working faces. The effectiveness of the method increases as the fracturing of the rock is growing. Nevertheless, air leakage due to positive pressure state can be a significant issue, even more if air doors are not well maintained. Infrastructure costs are relatively high, as an independent intake shaft has to be built, in addition to a return airshaft. On the contrary, in a state of negative pressure due to suction ventilation, where fresh air moves into the mine because the pressure is lower, the release of radon and progeny is speed up either because of the operations or the wall rock emission.

Development headings are areas of higher risk and their proper ventilation is critical. Auxiliary ventilation is to be used in such areas. Continuous air change should be planned for headings. During production, flow-through ventilation must be employed to keep the working staff in clean fresh air. Moreover, a forcing ventilation system should be used to deliver fresh air to the faces. This air from production areas is, of course, not to be reused to ventilate other areas. The distribution of pressure is harder to manage when multiple operations are taking place at the same time at various levels. Ideally, a retreat system should be implemented with a minimum possible number of working faces ventilated in series, decreasing the effective surface in intake airways. If this is not possible, then each mining area could be designed as an independent ventilation block. A split system of ventilation should be employed, in which fresh intake air is distributed to working blocks with respect to relative needs. Air from each section is afterwards collected in an isolated return airway without contaminating other active mining areas. The number of personnel required to work or travel in return airways should be kept to a minimum.

Beyond production areas, ventilation assessments should be made for all rooms and facilities in a rare earth underground mine. Primary airways should be kept free from mining activity, so that relatively high air velocities can be readily maintained. Air speed depends on local regulations. Mined-out areas should be kept on the return side of the ventilation system and be sealed whenever possible. Ramps are likely to be contaminated, for the airflow is not stable and is likely to change with the development of the mine. Conveyor ways, crushing facilities and ore passes in general should be ventilated so that exhaust air can be directed to the return air system quickly. Warehouses, repair shops and laboratories should be positively ventilated by controlled air volume flow rate. All unventilated areas in the mine must be sealed and marked, stating the hazard, to prohibit inadvertent entries. Moreover, to prevent radon flow from goaf areas or old drifts, hermetisation with sealing dams or concrete platforms in raise drifts should be evaluated. Last to consider is the maintenance of such a complicated system. Surveys and safety inspections are used to verify if the ventilation system is in compliance and if it meets all defined objectives. Determination of airflow and
the proof that the minimum limits are kept; evidence that air velocity is within the minimum and maximum limits; proof that the climate limits are met, are evaluations of primary importance. Any deficiencies found during an inspection should be acted upon promptly.

**Monitoring**

The principal objectives of monitoring are to evaluate occupational exposures with respect to the accepted standards and limitations and to provide data for adequate control. This can be done by collecting samples in short time periods, primarily in the working faces, where human exposure is more frequent. Thereby, there will be better detection and evaluation of the principal sources of exposure, assessment of the effectiveness of the control equipment, detection of anomalies in the mining operation and prediction of the effect of future operations on contamination levels.

**Personal protection measures**

Thorough personal hygiene should be required of all personnel and personal cleanliness should be mandatory at the end of each work shift. Resting and changing rooms should be isolated from working areas, and provided with convenient access to washing facilities. Personal protective equipment such as respirators, dust masks or air helmets should be used in areas where airborne dust is high or in exceptional circumstances when the ventilation has dropped down or during a maintenance task for which adequate ventilation is not available. Gloves should be worn for any direct contact with concentrates. Dosimeters should also be carried from all personnel.

**Groundwater assessments**

Confining water from coming in contact with airborne radon can be accomplished by using pipes for sealing or by applying grout covers ahead of development\(^\text{11}\) to divert water flow from the dust production areas. Furthermore, sufficient mine drainage can prevent the creation of stagnant pools of water contaminated with radon.

**Conclusions**

The presence of NORMs, especially of radon, is a paramount safety and health issue for the underground mining industry. This poses challenges for ventilation engineers to minimize the radiation contamination of the air and thus the human exposure. The most efficient methods to achieve control are; mechanical dilution ventilation, confinement or suspension of radiation source, dust reduction and control as well as personal protection measures. The improvements made so far have reduced radon concentration in underground mines, however, the work to further improve the evaluations continues. In an ideal underground rare earth mine radon accumulation is prevented and radiation concentration is kept to very low levels with respect to safety and cost efficiency. For this reason, a thorough investigation was made in this paper to evaluate the primary boundary conditions and requirements. What
can be done further on is to use these evaluations in order to build an overall assessment tool, to adjust and apply special techniques in mining of radon-emitting deposits.

References

A FRAMEWORK FOR THE SUSTAINABLE DEVELOPMENT OF RARE EARTH ELEMENTS MINING PROJECTS

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Abstract

The dependence of modern society on critical and/or strategic minerals such as Rare Earth Elements (REEs) is continuously growing due to the numerous end uses and other factors that have been recognized formerly. This paper proposes the adoption of a framework that can be used to guide extraction of REEs under Sustainable Development (SD) principles. The proposed framework includes fundamental elements that contribute to a holistic sustainable platform for REEs. It expands on the existing sustainable development framework and proposes: (a) five basic pillars: economy, society, environment, technology, and (geo)politics, (b) three controlling/limiting factors: policy, governance, and stakeholders, and (c) a number of output quantities to be used in decision making which can also be utilized as SD indicators.

Introduction

The significance of Rare Earth Elements (REEs) has been recognized in terms of their uses, their trade, the number of recent global initiatives, and the number of related geopolitical events/reports¹. Some of the findings are the following: China is considered a dominant player in REEs world production; the US, EU and Japan are the major importers of Chinese REEs; China’s demand for REEs is increasing; the main end uses of REEs include the energy and defense sectors; REEs applications may provide low cost efficient energy; since 2010 a large number of REE-related initiatives have been proposed within the EU and the US; the substitution of REEs is rare and/or impossible and/or in preliminary status; the recycling potential of REEs suffers by a number of constraints; and a significant number of critical geopolitical events/reports related to REEs have been identified since 2010. In addition, an effort was made to initiate a roadmap for the sustainable mining of REEs. This effort included the stream mapping of the REEs production process, the identification of stakeholders, and the detection of hazards/vulnerabilities of REEs mining². This effort was initiated since until that time there was a complete lack of such a roadmap. The substitution of REEs might be a difficult task, thus turning the problem of REEs substitution into a problem of “minimizing the amount of REEs (...) as little as will give the desired effect” to the end product³. The demand for REEs is expected to rise in the future⁴. In addition, the following demand related facts should be considered when someone is dealing with the sustainable development of REEs: (a) the world population is expected to increase⁵, (b) the global Gross Domestic Product (GDP) is also expected to increase⁶, and (c) the largest non-Chinese REEs mining companies are facing critical financial problems a few years after they started their operations⁷. Considering
all of the abovementioned information the complete global lack of a framework for the Sustainable Development of REE mining projects would seem a paradox. This paper discusses the adoption of a framework that can be used for guiding the Sustainable Development of REE mining projects.

**Sustainable Development Schematic Models**

The definition of Sustainable Development (SD) was established in 1987 by the “Brundtland Commission”10. In 1992, world leaders presented the principles of sustainable development at the United Nations Conference on Environment and Development in Rio de Janeiro, Brazil11. During that conference it was agreed that sustainable development consists of three elements: economic development, social development and environmental protection. Twenty years later, during the Rio+20 summit, it was concluded that “minerals and metals make a major contribution to the world economy and modern societies”12. A “sustainable path” was described as “one that allows every future generation the option of being as well off as its predecessors”13. Different schematic models picturing SD have been proposed: as ‘pillars’, as nested circles, or as overlapping circles14 (Figure 1).

![Figure 1: Different Description Models of Sustainable Development](image)

**Sustainable Development in the Minerals Industry**

In today’s world the challenge of sustainable mining is critical indeed. This was recognized in 2002 in the World Summit on Sustainable Development (WSSD), the Johannesburg Summit8. The Johannesburg summit enhanced “the contribution of mining, minerals and metals to
sustainable development” and called for actions “to address the environmental, economic, health and social impacts and benefits of mining” through the participation of stakeholders and encouraged world community to develop sustainable mining practices. In 2012, the United Nations RIO+20 Conference on Sustainable Development9 acknowledged that “mining activities should maximize social and economic benefits, as well as effectively address negative environmental and social impacts. In this regard, we recognize that Governments need strong capacities to develop, manage and regulate their mining industries, in the interest of sustainable development”.

Recognizing the need to move forward and develop REE mining projects in a sustainable manner, a framework for the SD of REEs mining projects is proposed in this paper. This framework is based on the concept of the “overlapping circles”, where the classic three-circle schema is complemented with more sustainability circles as well as a number of controlling/limiting factors/challenges that interact with or within the circles.

A Framework for the Sustainable Development of Rare Earth Elements Mining Projects

Today, the minerals sector and in particular the development REE mining projects are facing several challenges2.15. Any recommended action for the establishment of a sustainable mining framework should be within the context set off by the “Brundtland Commission”, the Rio Summit (AGENDA 21), and the Rio+20 recommendations. The proposed framework for the SD of REE mining projects includes fundamental elements that contribute to a holistic sustainable platform for REEs including:

✓ Five components represented as circles: economy, society, environment, technology, and (geo)politics.

✓ Three controlling/limiting factors: policy, governance, and stakeholders.

✓ A number of output quantities to be used in decision making: indicators

The recommended framework is pictured in Figure 2 and has a global application. To better encapsulate the concept of sustainable path, the “Swiss Cheese” model of accidents was adopted and adjusted to the scope of this analysis (Figure 3, left). Reason’s “Swiss Cheese” model has been proved to be a very useful tool in “accident” analyses: every “accident” is a result of “unsafe acts” created by decision makers and/or latent conditions16,17.
It is now broadly recognized that accidents in multifaceted conditions occur due to multiple causes that jointly interrelate resulting to the "accident". If the SD of REE mining project is considered as a desired multifaceted state that may contain several latent conditions then the ideal sustainable path should be determined, which produces the most efficient sustainability level without "accidents". The ideal sustainable path for the SD of REE mining projects is presented in Figure 3 (right).

The SD models pictured in Figure 1 have a significant weakness: it is difficult to quantify each criterion and its contribution to the overall scheme, since the models do not provide a measurable deviation of each probable sustainable metric entity (i.e. indices, ratios, indicators, etc.) from the ideal sustainable path. As a result, there is no meaningful interrelation/interconnection between the circles of SD and fuzziness is created for decision makers. To overcome this weakness the circles of sustainability should be examined from a different point of view, i.e., the vertical intersection of the circles should be studied (Figure 4).
Figure 3: Adjusted “Swiss Cheese” and Sustainable Development of REE mining projects (left) and Ideal Sustainable Path of REEs model (right)

Figure 4: Vertical intersection of the sustainability “overlapping” circles

The advantages of representing SD for REE mining projects are the following:

a. It provides better understanding of the SD interrelated elements.

b. It provides a more practical vision of the SD Path.
c. It provides the ability to measure the deviation of probable metric entities from the ideal SD Path.

d. It provides the ability to decision makers to avoid latent conditions of sustainability by reducing the deviations and make better decisions that will be closer to the ideal SD Path.

e. It clearly provides the “go-no-go” option to decision makers of mining projects by adjusting trade-offs between the different SD elements/metric entities.

f. It clearly sets up the relationship between stakeholders involved in the REEs SD, policy and governance.

Application of the generic framework in REEs Sustainable Development

A common expression in management says that “what gets measured gets done” 18. Evaluating REEs mining projects from the sustainability point of view is very critical for decision makers and all stakeholders because it can provide measurable positive or negative impacts of such projects. The best way to perform such evaluations is by using appropriate indicators. Thus, the core of the proposed framework (Figure 2) is based on indicators. The next step would be the development of a decision support system which will incorporate selected indicators and assist decision makers/stakeholders to better assess the impact of any REEs project from the sustainability point of view. A sustainability indicator can be defined as “a parameter, or a value derived from parameters, which points to, provides information about, describe the state of a phenomenon/environment/area, with a significance extending beyond that directly associated with a parameter value” 19. The selection of indicators should be based on the five proposed pillars of Figure 2. The overall process which details how the generic framework can be applied in the case of REEs is presented in Figure 5. The following attributes should be taken into consideration when selecting indicators:

1. The number of indicators is a considerable attribute. A large number of indicators could be difficult to manage and analyze.
2. The word “development” on itself implicates a dynamic process. Thus, the selected indicators shall be manageable and recordable through time.
3. Indicators shall be accessible at a reasonable time.
4. Indicators shall be pertinent to the geographical region exercised.
5. Indicators shall be easy to be communicated and reported.

Selected indicators for each of the five pillars are presented as examples:

✓ PILLAR 1 (Economy), Indicator: “Impact of the REEs project into the national/local economy” (income per person during operations and after mining finishes)

✓ PILLAR 2 (Society), Indicator: “Impact of the REEs mining project to prosperity in national/local society” (number of jobs created and/or level of unemployment during operations and after mining finishes)
PILLAR 3 (Environment), Indicator: “Impact of the REEs mining project to environment” (level of radionuclide activity concentrations during operations and after mining finishes)

PILLAR 4 (Technology), Indicator: “Impact of REEs mining project to the local high tech entrepreneurship” (number of high tech business permits issued by national local authorities during operations and after mining finishes)

PILLAR 5 (Geopolitics), Indicator: “Impact of REEs mining project to global secure supply of REEs” (percentage-reduction-of Chinese monopoly in global REEs production)

Figure 5: The process which describes how the generic framework can be applied in the case of REEs

Conclusions

In this paper a framework was proposed for the Sustainable Development of REE mining projects. This framework incorporated five basic “overlapping” circles: economy, society, environment, technology, and (geo)politics. The proposed framework also includes three controlling/limiting factors: policy, governance, and stakeholders, and indicators to be used in decision making. Furthermore, to better encapsulate the concept of sustainable path, the “Swiss Cheese” model of accidents was adopted. Finally, the “overlapping” circles of SD are proposed to be examined from their vertical intersection. This new approach provides a practical vision and better understanding of the SD Path, the quantification of the deviation from the ideal SD path, the “go-no-go” ability to SD decision makers and the ability to avoid latent SD conditions. Finally, it was explained hoe the generic SD framework can be applied in the case of REEs.
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Electrodeposition
SOLUBILITY OF RARE EARTH OXIDES IN MOLTEN FLUORIDES

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Abstract

The limited solubility of rare earth oxides (REOs) in fluoride melt has been an obstacle to preparation of rare earth metals (REMs) by oxide-fluoride electrolysis. However, very little work has been performed in this field. This paper presents a comprehensive analysis of the available data from previous publications. It reveals that the REO solubility increases with temperature and a linear relationship is obtained between the natural logarithm of the solubility and the reciprocal of the absolute temperature. The rare earth fluoride (RF₃) is crucial to REO dissolution and higher solubility is expected in melts with higher RF₃ content. The alkali fluoride (AF) can lower the melting points of binary systems and improve their electrical conductivity. The alkali earth fluoride (AF₂) can further lower the melting points and improve the stability of the melts.

Introduction

Thanks to the unique physical and chemical properties, rare earth elements are widely used in materials and consumer products, and their essential application in permanent magnets, lamp phosphors, rechargeable NiMH batteries has built a tight link to our modern life ¹.

The first attempt to prepare rare earth metals by electrolysis of an oxide-fluoride bath was as early as 1907 ². This was followed by many other investigations owing to the advantages of the process: low cost, environment-friendliness and easier handleability. The solubility of rare earth oxide in fluorides and in-depth understanding of the dissolution behaviour are both of fundamental and engineering importance for the design of electrolyte compositions and process operation. Unlike extensive studies on Al₂O₃-cryolite system ³⁻⁵, little work has been done for REO-fluoride melts. Even worse, there is inconsistency between results from different studies. This makes the access to reliable data more difficult.

Table 1 lists the major previous studies on solubility of rare earth oxides in molten fluorides. In the present paper, the data from these studies are summarised, reconstructed and analysed systematically for a better understanding of the influence of temperature and melt components on REO solubility in fluoride melts.
Table 1 Investigations on the solubility of rare earth oxides in fluoride melts

<table>
<thead>
<tr>
<th>Year</th>
<th>REO</th>
<th>Melt</th>
<th>Temperature, K</th>
<th>Solubility, mol. %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1961</td>
<td>La$_2$O$_3$</td>
<td>LiF-(BaF$_2$)-LaF$_3$</td>
<td>1223</td>
<td>0.61 - 0.78</td>
<td>Porter, 1961</td>
</tr>
<tr>
<td>1987</td>
<td>Nd$_2$O$_3$</td>
<td>LiF-NdF$_3$-MF$_2$ (M = Mg, Ca, Ba)</td>
<td>1273</td>
<td>0.14 - 0.96</td>
<td>Du, 1987</td>
</tr>
<tr>
<td>1991</td>
<td>Nd$_2$O$_3$</td>
<td>LiF-BaF$_2$-NdF$_3$</td>
<td>1073 - 1173</td>
<td>1.7 – 2.6</td>
<td>Wu, 1991</td>
</tr>
<tr>
<td>1994</td>
<td>Y$_2$O$_3$</td>
<td>LiF-YF$_3$</td>
<td>998 - 1273</td>
<td>0.26 – 2.1</td>
<td>Reddy, 1994</td>
</tr>
<tr>
<td>2002</td>
<td>Nd$_2$O$_3$</td>
<td>LiF-NdF$_3$-MgF$_2$</td>
<td>1023 - 1173</td>
<td>0.08 – 0.38</td>
<td>Stefanidaki, 2002</td>
</tr>
<tr>
<td>2008</td>
<td>Nd$_2$O$_3$</td>
<td>LiF-NdF$_3$</td>
<td>1323 - 1423</td>
<td>1.0 – 2.0</td>
<td>Hu, 2008</td>
</tr>
<tr>
<td>2012</td>
<td>La$_2$O$_3$, Sm$_2$O$_3$, Ho$_2$O$_3$</td>
<td>LiF/NaF/KF-ZrF$_4$</td>
<td>873 - 1073</td>
<td>0.039 – 0.73</td>
<td>Pshenichny, 2012</td>
</tr>
</tbody>
</table>

**Influence of different factors**

**Temperature**

Temperature is an unavoidable factor in studying a thermodynamic property. Figure 1a shows the dependence of the REO solubility in fluoride melts on the temperature. It is clear that the REO solubility increases with the increase in temperature.

The dissolution of REOs into fluoride melts can be simplified as an endothermal reaction

\[ \text{REO(s)} \rightarrow \text{REO(dissolved)} \]  (0)

The equilibrium moving to the right is favoured at higher temperature and consequently higher solubility of rare earth oxides is obtained in the melts.

In Figure 1b, the natural logarithm of the REO solubility in fluoride melts is plotted against the reciprocal of the absolute temperature for the same data as Figure 1a. It is obvious that most of the data can be interpreted by a linear relationship

\[ \ln \text{S}_{\text{REO}} = a \times \frac{1}{T} + b \]  (1)

where \( S_{\text{REO}} \) is the REO solubility in mol.% and \( T \) the temperature in K.

For example, the solubility of La$_2$O$_3$ in 51LiF-49ZrF$_4$ can be described using eq. (1) with \( a = -(5.4 \pm 0.2) \times 10^3 \) K and \( b = 4.5 \pm 0.2 \), with \( R^2 = 0.992 \), in the temperature range of 873 - 1073 K.
The fitting parameters for the rest of the systems are given in Table 2. Most of the plots have a $R^2$ with more than two nines, showing good linearity for these data sets. Meanwhile, the differences among the slopes and intercepts indicate the thermodynamic diversity of these systems. The parameters for the linear regression equation are exclusive to that specific system and it is not possible to extend them to an unknown system for solubility estimation. Nevertheless, these parameters are helpful for a more detailed study on thermodynamic features of the systems.

![Figure 1](image)

**Figure 1** Solubility of rare-earth oxides in fluoride melts as a function of temperature (reproduced with data from reference 7 - 12)

**Rare earth fluoride (RF₃) content**

Usually, a fluoride melt used to dissolve a rare earth oxide consists of the corresponding rare earth fluoride, an alkali metal fluoride, and sometimes an alkali earth metal fluoride, e.g. Nd₂O₃ in NdF₃-LiF-BaF₂. The RF₃ content, thus, is another essential factor to be considered.

Figure 2 shows the solubility of rare-earth oxides in fluoride melts as a function of rare earth fluoride content. Most of the published data give the same conclusion that the REO solubility increases with the RF₃ content in the melts except a set of data from Wu's study. As his work involved a ternary system, this disagreement could be attributed to the influence from BaF₂.
Table 2 Linear fitting parameters for data plots in Figure 1 (b)

<table>
<thead>
<tr>
<th>System</th>
<th>R²</th>
<th>a [10⁻³ K]</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₂O₃ in 80LiF-20YF₃</td>
<td>0.986</td>
<td>-4.1 ± 0.2</td>
<td>2.7 ± 0.2</td>
</tr>
<tr>
<td>Y₂O₃ in 75LiF-25YF₃</td>
<td>0.991</td>
<td>-4.4 ± 0.2</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td>Y₂O₃ in 60LiF-40YF₃</td>
<td>0.960</td>
<td>-5.2 ± 0.5</td>
<td>4.5 ± 0.4</td>
</tr>
<tr>
<td>La₂O₃ in 51LiF-49ZrF₄</td>
<td>0.993</td>
<td>-5.4 ± 0.2</td>
<td>4.5 ± 0.2</td>
</tr>
<tr>
<td>Sm₂O₃ in 51LiF-49ZrF₄</td>
<td>0.980</td>
<td>-5.9 ± 0.4</td>
<td>5.1 ± 0.4</td>
</tr>
<tr>
<td>Ho₂O₃ in 51LiF-49ZrF₄</td>
<td>0.969</td>
<td>-6.8 ± 0.6</td>
<td>6.2 ± 0.6</td>
</tr>
<tr>
<td>Nd₂O₃ in 77LiF-23NdF₃</td>
<td>0.987</td>
<td>-3.8 ± 0.2</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>Nd₂O₃ in 79LiF-6MgF₂-15NdF₃*</td>
<td>--</td>
<td>-4.5213</td>
<td>2.093</td>
</tr>
<tr>
<td>Nd₂O₃ in 66LiF-2BaF₂-32NdF₃</td>
<td>0.999</td>
<td>-4.69 ± 0.08</td>
<td>4.96 ± 0.07</td>
</tr>
<tr>
<td>Nd₂O₃ in 72LiF-2BaF₂-26NdF₃</td>
<td>1.000</td>
<td>-3.27 ± 0.01</td>
<td>3.63 ± 0.01</td>
</tr>
<tr>
<td>Nd₂O₃ in 77LiF-2BaF₂-21NdF₃</td>
<td>1.000</td>
<td>-2.03 ± 0.02</td>
<td>2.48 ± 0.02</td>
</tr>
<tr>
<td>Nd₂O₃ in 77LiF-20NdF₃</td>
<td>0.994</td>
<td>-3.3 ± 0.2</td>
<td>3.0 ± 0.1</td>
</tr>
<tr>
<td>Nd₂O₃ in 77LiF-50NdF₃</td>
<td>0.999</td>
<td>-4.47 ± 0.08</td>
<td>3.64 ± 0.06</td>
</tr>
<tr>
<td>Nd₂O₃ in 77LiF-42NdF₃</td>
<td>1.000</td>
<td>-6.29 ± 0.02</td>
<td>4.75 ± 0.01</td>
</tr>
</tbody>
</table>

* with only two data

Based on the study of Raman spectra of NdF₃-LiF-Nd₂O₃ system, Stefanidaki proposed a reaction between Nd₂O₃ and the molten NdF₃-LiF¹⁰:

\[
\text{Nd}_2\text{O}_3 + \text{NdF}_3 + 3(x-1)\text{LiF} = 3\text{NdOF}_{(x-1)}^+ + 3(x-1)\text{Li}^+
\]

This reaction shows that LiF acts only as a F⁻ ion donor, and that Nd³⁺ can support the REO dissolution process. He also pointed out that the most reasonable candidates of Nd-O-F complex seem to be NdOF₃⁺ and NdOF₅⁺ among the mononuclear compounds and Nd₂OF₁₀⁻ and Nd₂OF₁₄⁻ among the binuclear complexes¹⁰.

Hu described the Nd₂O₃ dissolution in the melt as a process in which the long-range order in Nd₂O₃ is destroyed by the interaction between O²⁻ and ion complex NdF₆⁻ and NdF₄⁻ to form NdOF₅⁻ or Nd₂OF₁₀⁻¹¹. Although the formula of the complexes is not exactly the same as Stefanidaki's, his finding confirmed the important role of NdF₃ content in Nd₂O₃ dissolution into molten LiF-NdF₃. The Nd-F ion complex increases with the content of NdF₃ in the binary system, which is beneficial to Nd₂O₃ dissolution¹¹,¹³.

Similar interaction of oxygen ions with RE-F complexes is expected in other REO-fluoride systems, resulting in a positive influence of RF₃ content on REO dissolution.
Figure 2 Solubility of rare-earth oxides in fluoride melts as a function of rare earth fluoride content (reproduced with data from reference 8 - 11)

Alkali metal fluoride (AF) content

The main purposes of an alkali metal fluoride addition are to lower the melting point of the electrolyte and improve the electrical conductivity.

The melting points of rare earth fluorides are all higher than 1400 K. Those of light lanthanide fluorides, the main elements prepared by molten salt electrolysis, are even as high as 1650 - 1766 K (see Table 3). However, the cell operation temperature is usually below 1400 K to secure smooth production and good quality and yield of final products. The addition of LiF can significantly lower the melting points of the melts. The eutectic points are 19 - 27 mol. % RF₃ (around 70 wt. %) and around 1000 K (see Table 3). The addition of NaF and KF can lower the melting points of the binary systems as well.

A study from Hu showed that the electrical conductivity of NdF₃-LiF melts increased with temperature and the LiF content. The radius of Li⁺ ion is much smaller than the other cations, resulting in lower resistance of its movement and higher mobility in the melt. Therefore, the conductivity is closely linked to the speed of Li⁺ ions and the obstruction of such complexes as NdF₆³⁻ and NdF₄⁻ to their movement under electric field. It is easy to figure out that the melts with the higher concentration of Li⁺ ions and less complex NdF₆³⁻ and NdF₄⁻ would have higher conductivity.
Table 3 Melting point of RF₃ and eutectic temperature of RF₃-LiF binary systems

<table>
<thead>
<tr>
<th>Fluoride</th>
<th>YF₃</th>
<th>LaF₃</th>
<th>CeF₃</th>
<th>PrF₃</th>
<th>NdF₃</th>
<th>SmF₃</th>
<th>GdF₃</th>
<th>DyF₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point *, K</td>
<td>1421</td>
<td>1766</td>
<td>1710</td>
<td>1672</td>
<td>1650</td>
<td>1579</td>
<td>1504</td>
<td>1427</td>
</tr>
<tr>
<td>Eutectic temperature (RF₃-LiF) **, K</td>
<td>968</td>
<td>1043</td>
<td>1028</td>
<td>1023</td>
<td>1011</td>
<td>971</td>
<td>973</td>
<td>973</td>
</tr>
</tbody>
</table>

* data from reference 17
** data from reference 14

Since higher REO solubility can be obtained in melts with higher RF₃ content, the AF content in a binary melt (xₐF = 1 - x₉₃) should have a negative effect (see Figure 2).

Pshenichny compared solubility of lanthanide oxides in fluorozirconate melts and found that the solubilities decrease in the increasing order of Ln³⁺ ion radius, i.e. S₉₃ > S₁₅ > S₂₁, and in the increasing order of alkali metal cation radius in the melts, i.e. S₉F > S₅₄ > S₆K (see Figure 3). This is consistent with the results from Ambrová. The acidic power of a cation Z was calculated and used to interpret the dissolution behaviour of oxides in the melts. The acidic power of binary systems decreases sequentially as the cationic radius of alkali metal increases. The decrease in solubility of lanthanide oxides can then be associated with the decrease in polarizing power of the cation.

![Figure 3 Solubility of lanthanide oxides in fluorozirconate melts (reproduced with data from reference 12)](image)

**Alkali earth metal fluoride (AF₂) content**

The addition of AF₂ in the melts can further lower their melting points together with limiting the evaporation of LiF and lowering the melt viscosity.
Wu investigated the melt composition before and after dissolution tests and confirmed the positive impact of BaF$_2$ on preventing evaporation of LiF due to the formation of complexes.

Figure 4 shows the influence of AF$_2$ addition on the REO solubility in LiF-MF$_2$-NdF$_3$ melts (M = Mg, Ba). In some cases it has a positive effect while sometimes negative, but the variations are moderate. This suggests that the REO solubility should stay low and stable with AF$_2$ addition. It could be meaningful in some cases. For example, Nd-Mg alloy prepared by co-electrowinning from an LiF-MgF$_2$-NdF$_3$ melt containing dissolved Nd$_2$O$_3$ should be possible as the low solubility of Nd$_2$O$_3$ is not reduced by the MgF$_2$ addition.

![Figure 4 Solubility of Nd$_2$O$_3$ in LiF-MF$_2$-NdF$_3$ melts (M = Mg, Ba) (reproduced with data from reference 8 and 10)](image)

**Conclusions and future work**

This paper comprehensively summarises, reconstructs and analyses the available data from previous publications on the REO solubility in molten fluorides. The REO solubility increases with temperature and RF$_3$ content. There is a simple linear relationship between the natural logarithm of the solubility and the reciprocal of the absolute temperature. The alkali metal fluoride addition, mostly LiF, can lower the melting points of binary systems and improve their electrical conductivity. The alkali earth metal fluoride, usually as a third additive, can further lower the melting points and limiting the evaporation of LiF.

As a key factor for optimized electrolysis, study on the REO solubility can help the electrolyte selection and feed rate control. A more detailed analysis of the solubility data is needed to find out a method for estimation of the solubility on the basis of thermodynamic calculations, which would assist selection of electrolyte, aiming for a higher REO solubility without
compromising other electrolyte properties (e.g. viscosity, electrical conductivity). More work should be done on the structure of the REO-fluoride system to reveal the mechanism of REO dissolution. Studies on dissolution kinetics will enable a better feed rate control to lead to a smoother cell operation.

Acknowledgement

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References
ELECTRODEPOSITION OF RARE EARTH METALS IN IONIC LIQUIDS

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Abstract

In this paper the available literature on the application of ionic liquids in rare earth metals electrodeposition, is briefly discussed and the main electrochemical properties of ionic liquids, in relation with such applications, are presented. In addition, the results of a preliminary investigation for the suitability of pyrrolidinium-based ionic liquids on the electrodeposition of lanthanum are presented.

Introduction

Production of rare earth metals and alloys are conventionally performed by high temperature molten salts electrolysis, which creates highly corrosive environment and demands high energy consumption. Recently, the use of organic solvents has been implemented for the electrodeposition of rare earths; however they were considered inadequate, due to their high volatility and their inflammability.

Ionic liquids gain increasing attention in the recent years, as electrolytes for the recovery of metals more electropositive than hydrogen. It concerns for salts that are generally liquid at ambient conditions, consisting of a bulky organic cation and a smaller organic or inorganic anion \[1\]. The variety, the combination, the position and the size of cations and anions adjust remarkable properties for ionic liquids, such as very low melting point, high chemical and thermal stability, negligible vapour pressure, ability to dissolve a wide range of organic and inorganic compounds, important ionic conductivity and broad electrochemical window \[2\]. These properties of ionic liquids, in combination with the non-flammability they present, render them advantageous for the electrodeposition of rare earth metals, in comparison with the organic solvents currently used \[3-5\].

Preliminary studies have proven that ILs are capable solvents and electrolytes of reactive metals, such as Li, Na, Al, Mg \[6-8\]. In this paper the applications of ionic liquids in the electrodeposition of rare earth metals are reviewed and preliminary results of the electrodeposition of lanthanum are presented.
Electrodeposition of rare earths in ionic liquids

The electrodeposition of rare earth elements from ionic liquids has been mainly investigated with four different families of ionic liquids based on their cation. It concerns for imidazolium, pyrrolidinium, ammonium and the phosphonium-based ionic liquids with a variety of anions.

Imidazolium-based ionic liquids

It is the most widely investigated family of ionic liquids for metals electrodeposition. Especially, the imidazolium chloroaluminate systems have been used successfully for the electrodeposition of Al and refractory metals such as Ta.

In the case of reduction of rare earth metals from imidazolium-based ionic liquids, Tsuda et al. [9-10] reported the co-deposition of La with Al from a LaCl₃-saturated Emim-AlCl₃ system with excess of LiCl and SOCl₂ and not in pure Emim-AlCl₃. The lanthanum content of the resulted Al-La alloy was 0.05% up to 0.50%, in terms of mass fraction. In addition, the co-deposition of La-Co alloys was studied in the ionic liquid Bmim-CF₃SO₃ using copper coils as cathodes [5]. Moreover, the co-deposition of Sm and Co in BmimBF₄ was reported [5], through inductive effect and the content of Sm in the final alloy was estimated between 5% and 40%.

Lin [11] et al in 1993 approached the electrochemical behaviour of Ce(III)/Ce(IV) couple in the basic aluminium system (AlCl₃ – MeEtimCl) and via ultraviolet-visible spectroscopy it was stated that Ce(III) and Ce(IV) form complexes such as [CeCl₆]ₓ⁻, whereas x=3 and 2 respectively. Jagadeeswara et al. [12] researched the electrochemistry of the systems Ce(III), Sm(III) and Eu(III)/Eu(II) in BmimCl. The application of cyclic voltammetry and chronopotentiometry at platinum working electrode revealed the reduction of trivalent Ce and Sm ions to the divalent state at various temperatures and found them to be quasi-reversible reactions. In 2006, Yamagata et al. [13] studied the electrochemical behaviour of redox reactions Sm(III)/Sm(II), Eu(III)/Eu(II) and Yb(III)/Yb(II) in the ionic liquid Emim-TFSI through cyclic voltammetry and it was found to be quasi-reversible or irreversible.

Pyrrolidinium-based ionic liquids

Glukhov et al. [14] have stated the reduction of Y, Gd and Yb in the ionic liquid BMP-CF₃SO₃ on both, platinum and copper electrodes. On the voltammetric curves performed with the Pt electrodes in the systems Y and Gd with this IL, the observed cathodic peak with a maximum value of -2.6 V (rel. Ag/0.1 M Cl⁻) was attributed to the reduction of the trivalent cations to the metallic state. The electrodeposition of these metals was performed under potentiostatic or galvanostatic conditions and a tenuous black precipitate was formed on the electrode’s surface. It was also shown that the reduction of Yb(III) to the metallic form occurs step by step via Yb(II) formation and the limiting stage of the cathodic process is the adsorption of the metal cation on the electrode. Legeai et al. [15] have shown that the reduction of La in OMP-TFSI is an irreversible reaction and that La electrodeposition in this ionic liquid under
potentiostatic polarisation conditions -1.5 V (vs Ag/AgCl), for 120 min, at 298 K, resulted in the cathodic deposit of a thick La film of 350 nm. In addition, Yamagata et al. [13] studied by cyclic voltammetry the redox reactions of the Sm(III)/Sm(II) couple in BMP-TFSI ionic liquid using a glassy carbon electrode and determined the redox reactions as quasi-reversible or irreversible. They also studied the electrochemistry of Yb(III) in BMP-TFSI by cyclic voltammetry and concluded to a cathodic and an anodic peak at around -0.95 V (vs Ag/Ag⁺), which considered attributable to the reduction of Yb(III) and the oxidation of Yb(II), respectively. The electrochemical behaviour of Eu(III) in BMP-TFSI was researched by Rao et al. [16] with glassy carbon and stainless steel electrodes, at various temperatures. The cyclic voltammograms revealed a quasi-reversible behaviour of the redox couple Eu(III)/Eu(II) and an irreversible behaviour of the couple Eu(II)/Eu(0), which presented a cathodic peak attributed to the reduction of Eu(II) to the metallic state. In the same ionic liquid (BMP-TFSI) that contained also chloride anions, Hussey et al. [17] studied the electrochemical and spectroscopic behaviour of Nd(III) and Pr(III). According to their results, the electrolytic dissolution of both metals in this ionic liquid’s system produces only the respective trivalent cations, which can be reduced to the Ln²⁺(II) state, but the resulting divalent species exhibit only transient stability, undergoing rapid disproportionation to Ln³⁺(III) and Ln⁰ states.

**Ammonium based ionic liquids**

Glukhov et al. [14] investigated the reduction of Y, Gd, Yb in the ionic liquid Bu₃MeN-CF₃SO₃ and concluded that the deposition of the above metals is only possible on a copper substrate and does not occur on a platinum one. Bhatt et al. [18] reported the reduction of selected lanthanide cations (La, Sm and Eu) to the zero-valent state in the ionic liquid Me₃NBu-TFSI. The lanthanide cations were introduced to the ionic liquid as the TFSI hydrate complexes. Cyclic voltammograms revealed a cathodic peak at -2.4 V vs Fc⁺/Fc for the lanthanum system attributed to the reduction to metallic state, whereas two peaks were observed for Sm- and Eu- systems, the less negative were associated with (III)/(II) reaction and the more negative with the reduction to the metallic state.

**Phosphonium based ionic liquids**

In 2008 Matsumiya et al. [19] studied the electrochemical behaviour of Sm(III) in the phosphonium based ionic liquids. The diffusion coefficients of Sm(III) were determined via cyclic voltammetry, chronoamperometry, chronopotentiometry and were estimated to be on the order of 10⁻⁹ cm²s⁻¹. It was stated that the trivalent samarium complexes in the phosphonium based ionic liquids were assumed to present higher ion mobility in respect to those in the ammonium ionic liquids, due to weaker interaction between the cation and the anion in phosphonium-based ILs. In addition, Kondo et al. [20] researched the suitability of P[225]-TFSI for the electrodeposition of neodymium. The diffusion coefficient of Nd(III) was investigated by chronopotentiometry with cylindrically symmetrical diffusion and was estimated on the order of 10⁻¹¹ m²s⁻¹ at 100 ºC. The cyclic voltammograms of Nd(III)/P[225]-
TFSI containing 0.5 mol dm\(^{-3}\) NdTFSI\(_3\) presented an anodic and a cathodic peak currents that were attributed to the oxidation and the reduction of Nd(III), respectively. The reduction of Nd cation was observed at -2.5 V vs a platinum wire immersed in the solution used as a quasi-reference electrode, compensated for the Fc\(^+/\)Fc redox couple. The electrodeposition of neodymium in the specific ionic liquid was performed by potentiostatic electrolysis at -3.1 V vs Fc\(^+/\)Fc at 150 °C. A black electrodeposit was fine and formed uniformly neodymium particle and was observed by SEM and identified from the evaluation of EDX.

Moreover, the electrochemical behaviour and electrodeposition of dysprosium (Dy) in the phosphonium-based ionic liquid P\(_{225}\)-TFSI were investigated by Kurachi et al. [21]. The cyclic voltammetric measurements resulted in one step reduction of the trivalent dysprosium ion in phosphonium-based ionic liquid. On the other hand, no anodic peak ascribed to the oxidation of dysprosium metal was observed in this electroanalytical study. The diffusion coefficient and the activation energy for diffusion of the trivalent Dy complex in this IL were also estimated, using semi-integral analysis. The diffusion coefficient of Dy(III) was calculated to be 2.0×10\(^{-12}\) m\(^2\)s\(^{-1}\) at 25 °C, closed to that of the trivalent lanthanoid ion such as Eu(III) and Sm(III) in phosphonium-based ionic liquids. In addition, the activation energy for diffusion was estimated to be 65 kJmol\(^{-1}\) (0.5 M) and 49 kJmol\(^{-1}\) (0.075 M).

**Chlonine based ionic liquids**

In 2012 Ishii et al. [22] investigated the physical and electrochemical properties of choline-based ionic liquids and their capacity to reduce iron and neodymium cations. The novel cationic blended ionic liquids which were constituted by the 2-hydroxyethyltrimethylammonium bis(trifluoromethylsulfonylimide Ch-TFSI and P\(_{225}\)-TFSI was applied for the electro-recovery of neodymium. In this study the starting materials were voice coil motors for hard disk drivers and the electrodeposits obtained were examined by SEM/EDX and XPS. According to the results of this study, iron group and rare earth metals can be recovered separately by electrodeposition in two stages.

**Preliminary studies on lanthanum electro-recovery from pyrrolidinium-based ionic liquids.**

Experimental work of the specific research focused on evaluating the use of pyrrolidinium-based ionic liquids for the electro-recovery of reactive metals, such as the Rare Earth Metals are. More precisely, the reduction of lanthanum in the ionic liquid N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonylimide (BMP-TFSI) was studied, at room temperature. BMP-TFSI was selected among the different pyrrolidinium-based ionic liquids, because it presents electrochemical stability under cathodic polarisation, satisfying ionic conductivity and it is an air and water stable electrolytic medium.

**Materials and apparatus**

The ionic liquid BMP-TFSI was supplied by Solvionic and Lanthanum nitrate hexahydrate was purchased by Alfa Aesar. The lanthanum nitrate salt was heated at 100 °C under vacuum for
72 h and was dissolved in pure acetone, where subsequently the proper amount of electrolyte was added to form a solution's concentration of the order of 0.06 M. The solution was placed at 60 °C under vacuum for approximately 2 h to remove acetone and then at 100 °C under vacuum for 24 h to remove residual water.

Linear and cyclic voltammetry tests were performed in a three microelectrodes cell (PAR) connected to a VersaSTAT3 potentiostat (PAR); the obtained experimental data were analysed with the VersaStudio software (PAR). The working electrode was a platinum disk of d = 1.98 mm, as a counter electrode a Pt wire immersed directly into the solution was used and finally, as a reference electrode the redox couple Ag/0.1 M AgNO₃ in acetonitrile was employed. The working electrode was polished with aluminum paste 1 μm on a velvet pad and electrochemically in 1 M sulfuric acid. Although BMP-TFSI exhibits hydrophobic characteristics and it is stable under normal atmospheric conditions, the cyclic voltammetry and chronoamperometry measurements were performed in a glove box, providing an inert atmosphere by purging nitrogen gas to minimise oxygen and moisture contamination. The morphology of electrodeposits was examined by Scanning Electron Microscope (JEOL6380LV), provided with Energy Dispersive Spectrometry.

**Results**

The electrochemical window was determined at room temperature by cyclic voltammetry and the cathodic limit of the electrolyte was determined at -3.5 V vs Ag/Ag⁺. Figure 1 shows the cyclic voltammogram recorded in the system BMP-TFSI/La. As it is obvious, a generation of an intense cathodic peak begins at -2.2 V vs Ag/Ag⁺, attributed to the reduction of trivalent lanthanum cation (La³⁺) to the metallic state. The absence of corresponding anodic peak on the reverse scan allows the assumption that lanthanum reduction is irreversible [15]. Moreover, the cathodic peak at -1 V is ascribed to the limited reduction of hydrogen cations, due to slight moisture [2] that inevitably was present and the narrow shoulder at -1.5 V is attributed to an adsorption La³⁺ reaction occurring on the electrode, prior to the reduction of lanthanum [14, 15].
Figure 1: Cyclic voltammograms recorded with scan rate 20mV/s vs Ag/Ag⁺ on a Pt electrode at 25 °C: (1) BMP-TFSI and (2) for the solution of 0.06 M La(NO₃)₃ in BMP-TFSI.

Furthermore, the electrodeposition of lanthanum was realised on a copper substrate, under potentiostatic conditions for 5 h at -3.1 V (vs Ag/Ag⁺) at 25 °C. The electrodeposits were examined in SEM and EDS analysis (Figure 2) revealed the electrodeposition of lanthanum. The EDS analysis also revealed the existence of fluorine and sulfur that may occur, due to the TFSI anion adsorption on the electrode’s surface that could explain the absence of anodic peak.

Figure 2: SEM image depicting the electrodeposits of lanthanum(left), EDS analysis of the electrodeposits(right)
Conclusions

Ionic liquids are promising electrolytes, suitable for the electrodeposition of rare earth metals. The research in this area has proven their ability to reduce and to permit the electrodeposition of drastic metals, without the drawbacks present in the currently used technology. The preliminary electrochemical investigation of BMP-TFSI revealed its potential use for reduction of lanthanum and appears, due to its physicochemical properties, to be an appropriate medium for the electrodeposition of rare earth elements.

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ELECTROCHEMICAL RECOVERY OF RARE EARTH ELEMENTS FROM MAGNET SCRAPS- A THEORETICAL ANALYSIS

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Abstract

Recovery of rare earth elements (REEs) from secondary resources is of great environmental and economic importance. In the case of magnet scraps, multi-step hydrometallurgy and liquid metal extraction with high energy consumption are usually applied to accomplish acceptable recovery rate of REEs from the scrap. This paper aims to provide theoretical framework for using electrochemistry to selectively extract REEs into aqueous solution. Thermodynamic and electrochemical behaviour of different components in the alloy are theoretically predicted and correlated with available data from the literature. The role of microstructure and different elements in dissolution mechanism of the REE magnet is reviewed. Through understanding various factors involved in dissolution behaviour of the alloy, an electrochemical process with enhanced selectivity to recover REEs can be established.

Introduction

Rare earth elements are of great importance in modern industry for producing various functional materials like permanent magnets, rechargeable batteries, catalysts, lamp phosphors because of their unique magnetic and electronic properties. Due to the increased demand and supply shortage, REEs are listed as critical raw materials of strategic importance in many countries in the world\textsuperscript{1-2}. This has promoted research for recovering REEs from end-of-life (EOL) products and the scrap created during production. Neodymium iron boron magnet (Nd\textsubscript{2}Fe\textsubscript{14}B) is one of the major usages for rare earth elements and has 62\%\textsuperscript{3} of the market share of permanent magnetic material. Apart from neodymium, REEs like dysprosium and praseodymium are used in varying amounts (in total 25-30\%) for obtaining required magnetic properties\textsuperscript{4}. Cobalt (0-10\%) is often added to increase the Curie temperature and other elements like vanadium, oxygen and nitrogen can be added in trace amounts to reduce corrosion\textsuperscript{5a,5b}.

The complex composition of EOL magnets and magnet scrap makes the recovery of REEs rather difficult and demands a range of metallurgical and chemical techniques. Various methods have been reported in the past for recovering neodymium and other rare earth
elements from the magnets. Lyman et al.\textsuperscript{6} used the leaching method and have obtained high recovery of neodymium (98\%) by dissolving the scrap in sulfuric acid followed by using alkali hydroxides to precipitate double salts of neodymium which can be further treated to obtain neodymium oxide. Other research groups have also tried selective leaching\textsuperscript{7}, ultrasound-assisted leaching\textsuperscript{8} and a combination of pre-roasting the scrap along with selective leaching and solvent extraction\textsuperscript{9} to recover the REEs from the scrap. Although the above mentioned hydrometallurgical methods have achieved appreciable recovery of REEs, they require multiple steps to enhance leaching selectivity, expensive pre-treatment techniques and consumption of large amounts of chemicals. Hence for an aqueous chemical method to be economically viable for recycling, enhanced selectivity of REEs recovery combined with low consumption of chemicals and reduced number of steps involved is of paramount importance.

In this paper, the thermodynamics and the corresponding electrochemical behaviour of various elements present in waste magnets are discussed and compared during dissolution into an aqueous solution. With improved understanding of these behaviour, a process to selectively extract REEs from waste magnet can be established.

**Thermodynamic evaluations**

A typical composition of commercial magnet and magnet scraps obtained from literature\textsuperscript{9,10,11} is listed in Table 1.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Nd</th>
<th>Dy</th>
<th>Pr</th>
<th>Fe</th>
<th>B</th>
<th>Co</th>
<th>C</th>
<th>N</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>23-25</td>
<td>3.5-5</td>
<td>0.05-5</td>
<td>62-69</td>
<td>1</td>
<td>0-10</td>
<td>0-0.14</td>
<td>0-0.1</td>
<td>1-2</td>
</tr>
</tbody>
</table>

*Others- Cu, Al, Ga, Si, Gd, Mo.

The standard Gibbs energy of formation for different rare earth species are calculated from the literature\textsuperscript{12,13} and their corresponding Nernst equation are summarized in Table 2. It can be noticed that the standard electrode potentials \((E_{\text{RE}}^{3+/2} = -2.2 \text{ to } -2.4 \text{ V vs SHE})\) of the rare earth elements are very close owing to their similar chemical nature.

**Table 2:** Calculated values of \(\Delta G^0\) (kJ/mol) and standard reduction potential at 298 K and the corresponding Nernst equation. Soluble species concentrations (except H\(^+\)) is \(10^{-1.0}\) M
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$E^\circ$ (V)</th>
<th>Nernst equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Nd}^{3+} + 3e^- \iff \text{Nd}$</td>
<td>-671.6</td>
<td>-2.32</td>
<td>$E = -2.32 + 0.020 \log [\text{Nd}^{3+}]$</td>
</tr>
<tr>
<td>$\text{Nd} + 3\text{H}_2\text{O} \iff \text{Nd(OH)}_3 + 3\text{H}^+ + 3e^-$</td>
<td>-563.3</td>
<td>-1.94</td>
<td>$E = -1.94 + 0.059 \text{pH}$</td>
</tr>
<tr>
<td>$\text{Nd}^{3+} + 3\text{H}_2\text{O} \iff \text{Nd(OH)}_3 + 3\text{H}^+$</td>
<td>108.3</td>
<td></td>
<td>$3 \text{pH} = 19 - \log [\text{Nd}^{3+}]$</td>
</tr>
<tr>
<td>$\text{Dy}^{3+} + 3e^- \iff \text{Dy}$</td>
<td>-664.0</td>
<td>-2.29</td>
<td>$E = -2.29 + 0.020 \log [\text{Nd}^{3+}]$</td>
</tr>
<tr>
<td>$\text{Dy} + 3\text{H}_2\text{O} \iff \text{Dy(OH)}_3 + 3\text{H}^+ + 3e^-$</td>
<td>-564.4</td>
<td>-1.95</td>
<td>$E = -1.95 + 0.059 \text{pH}$</td>
</tr>
<tr>
<td>$\text{Dy}^{3+} + 3\text{H}_2\text{O} \iff \text{Dy(OH)}_3 + 3\text{H}^+$</td>
<td>98.6</td>
<td></td>
<td>$3 \text{pH} = 17.3 - \log [\text{Dy}^{3+}]$</td>
</tr>
<tr>
<td>$\text{Pr}^{3+} + 3e^- \iff \text{Pr}$</td>
<td>-680.3</td>
<td>-2.35</td>
<td>$E = -2.35 + 0.020 \log [\text{Pr}^{3+}]$</td>
</tr>
<tr>
<td>$\text{Pr} + 3\text{H}_2\text{O} \iff \text{Pr(OH)}_3 + 3\text{H}^+ + 3e^-$</td>
<td>-568.0</td>
<td>-1.96</td>
<td>$E = -1.96 + 0.059 \text{pH}$</td>
</tr>
<tr>
<td>$\text{Pr}^{3+} + 3\text{H}_2\text{O} \iff \text{Pr(OH)}_3 + 3\text{H}^+$</td>
<td>111.9</td>
<td></td>
<td>$3 \text{pH} = 19.68 - \log [\text{Pr}^{3+}]$</td>
</tr>
</tbody>
</table>

Their very negative potential values which fall below the hydrogen evolution line indicate a strong reactivity in aqueous solutions. Experimental observation of corrosion and passivity behaviour of neodymium in different conditions have also confirmed rigorous hydrogen evolution\textsuperscript{14}. In particular, comparison of the behaviour of iron and REEs in aqueous solution at different pH can be of importance. Koyama et al.\textsuperscript{15} used a Pourbaix diagram (Fig. 1) to see stability of different species of neodymium and iron in different pH and they selectively leached out Nd\textsuperscript{3+} by leaving out iron as Fe\textsubscript{2}O\textsubscript{3} in the solution.

In contrast to selective leaching where pH plays a vital role, using scrap magnets in an electrochemical cell offers an additional advantage of controlling parameters like potential and current density to manipulate and selectively dissolve REEs. Fig. 2 shows standard electrode potentials of different components of scrap magnets vs Ag/AgCl electrode (0.25 V vs SHE). The other major elements present in the waste magnets in terms of weight percentage are iron and cobalt. The standard reduction potentials of iron and cobalt are -0.44 V and -0.28 V vs SHE respectively. EOL magnets also contain copper, as a minor additive or in the coating along with nickel to prevent corrosion.
It can be noted that, when magnets are deployed as anodes in a 3-electrode electrochemical cell (Ag/AgCl reference electrode), selective dissolution can be accelerated by controlling the potential and maintaining it in the region between dissolution of rare earths and the region in which metallic iron, cobalt and other elements are stable. Further anodic polarization of the scrap magnets can accelerate the dissolution process.

Fig. 2: Standard reduction potential (V vs Ag/AgCl) of different elements in scrap magnet\textsuperscript{9a}
Analyzing elements individually can theoretically form a basis for selective dissolution but dissolution of individual components from an alloy is governed by their partial thermodynamic properties. Partial potential of an individual component in an alloy can be written as

\[ E_i^M = -\left(\frac{RT}{Z_iF}\right) \ln N_i \] (1)

where \( E_i^M \) is the difference between equilibrium electrode potential of the component \( i \) in the alloy and the corresponding potential of the same component in the individual phase. \( R, T, F, Z_i, N_i \) are molar gas constant, temperature, Faraday’s constant, number of electrons transferred and molar fraction of the component respectively. By definition mole fraction is less than one and hence the partial potential of a component in the alloy will always be more positive than the individual component potential. Hence experimental determination of the extent of positive shift for individual components in the Nd\(_2\)Fe\(_{14}\)B alloy in different electrolytic environments is vital.

An electrolyte environment which is non-inhibiting and encouraging free corrosion process is essential. Passivity is in principle possible in highly alkaline solutions and Song et al.\(^{17}\) observed that NdFeB magnets form passive hydroxide layers in sodium hydroxide and in oxalic acid. Jingwu et al.\(^{18}\) observed similar type of passive behaviour in phosphoric acid with low corrosion current. However the alloy freely dissolves in other acids such as sulfuric acid, nitric acid and hydrochloric acid with high current density and is also susceptible to attack by chloride and other ions even in the solutions in which they exhibit passivity. Hence for active dissolution of the magnets it is preferred to have an acidic conditions with strong acids having high corrosion current.

**Microstructure of the magnet and dissolution mechanism**

Another crucial aspect of selective dissolution is to understand the correlation between microstructure of the alloy and the corresponding dissolution mechanism. NdFeB magnets have a matrix ferromagnetic phase (Φ) of Nd\(_2\)Fe\(_{14}\)B tetragonal compound and is surrounded by intergranular regions containing a neodymium rich phase (n) and a boron rich phase (η)\(^{19}\). The complexity of the intergranular region in the microstructure of the neodymium magnets depend upon the additional elements such as cobalt, aluminum and gallium. In order to selectively dissolve rare earths, an understanding of dissolution mechanism in different environments is thus necessary. Several authors\(^{19,20,23}\) have proposed that neodymium rich
phases (n) corrode preferentially due to the formation of a galvanic couple owing to negative standard potential of rare earths. This is followed by the boron rich phase dissolution and this renders the matrix loose finally creating disruption of the matrix phase. Corrosion in Nd-Fe-B alloy is a natural process and can even result in the pulverization of the magnet. The scheme of step by step dissolution process presented by Schlutz\textsuperscript{19} et al. is given in Fig. 3.

![Fig. 3: Schematic illustration of dissolution process of Nd-Fe-B magnets by corrosion\textsuperscript{19}](image)

Mao et al.\textsuperscript{20} observed the dissolution process of individual phases by synthesizing them separately and subjecting them to different corrosion tests. The Nd rich phase had the most negative open circuit potential followed by matrix phase and the boron rich phase, indicating that the Nd rich phase has the highest electrochemical reactivity. These results further strengthen the conclusion that selective dissolution of rare earths are feasible and is in fact a naturally occurring corrosion process.

The composition of different components in the alloy also play a crucial role in dissolution process. Corrosion studies of magnets with higher weight percent of iron in phthalate buffer showed reduced current density, indicating formation of passive layers like iron oxide preventing corrosion\textsuperscript{21}. Aluminum, gallium and copper have reduced the corrosion as they reduce the strength of galvanic coupling among magnetic phases\textsuperscript{22} and cobalt has been observed to improve corrosion resistance as it prevents magnetic pulverisation\textsuperscript{23}. High rate of dissolution is observed in low carbon and oxygen alloy when the nitrogen content exceeds 0.1 wt\%. Oxygen impedes corrosion when it is added between 0.6-1.2 wt\% and the optimum amount of carbon was found to be 0.1wt\% as anything above that facilitates corrosion\textsuperscript{5a}. Dysprosium and niobium have been said to have formed stable intermetallic phases which retards corrosion\textsuperscript{24} but also high amount of dysprosium (16 \%) has been deemed as disadvantageous \textsuperscript{25}. On the whole, it is important to know the nature of the scrap to accelerate the dissolution process by various means and by altering the environment.
**Electrochemical cell: cathode products and anode slime**

Table 2 lists the possible anodic reactions in the electrochemical cell. Besides dissolution of rare earth metals, co-dissolution of iron and cobalt by chemical or electrochemical means is also possible although not desirable.

Rare earths, due to their very negative potential liberate hydrogen on the cathode in aqueous solutions from an electrochemical process. Due to the same, the rate determining step becomes mass transport as the charge transfer is relatively fast. The cathodic reactions in such case are

\[
2\text{H}^+ + 2\text{e}^- \Leftrightarrow \text{H}_2 \quad (2)
\]

\[
\text{M}^{n+} + \text{n} \text{e}^- \Leftrightarrow \text{M} \quad (3)
\]

\[
2\text{H}_2\text{O} + 2\text{e}^- \Leftrightarrow \text{H}_2 + 2\text{OH}^- \quad (4)
\]

Hydrogen evolution reaction though inevitable, can be kinetically slowed down with proper choice of a cathode as it will hinder deposition of non-REEs as well as modify the pH. Schlutz et al.\textsuperscript{14} observed water reduction to be the prominent cathodic reaction for pure neodymium at lower concentrations (≤0.01 M) and at higher concentrations they observed hydrogen evolution. In addition to just acting as counter electrode, the cathode can also be chosen in such a way that it allows deposition of co-dissolved non-REEs. In order to have a cathode to allow deposition of non-REEs, it should a) be inexpensive b) have slow kinetics and low exchange current density for hydrogen evolution reaction c) favor the deposition of non-REEs like iron, nickel or cobalt. Besides if such a deposit from scraps can also be attractive in terms of commercial applications (such as FeNi alloys) it can be an added benefit.

A simple schematic is illustrated in Fig. 4 for the conceptual framework of the electrochemical cell described in the paper. Fig. 4 a) shows the scrap magnets placed as anodes in a simple 2-electrode electrochemical cell.
Fig. 4 Simple schematic of the proposed electrochemical method for REE recovery

Fig. 4 b) shows an in-progress dissolution. Although it is preferred to selectively dissolve only rare earth ions, chemical dissolution and the complex microstructure of the alloy might also encourage co-dissolution of non-REEs. These co-dissolved non-REEs can be further deposited back on the cathode which results in a partially purified solution enriched in rare earths which is suitable for further elemental recovery and the rest of undissolved elements can be collected as anode slime. The proof of principle experiments are currently in preparation.

Conclusion

This paper establishes the theoretical framework required to perform an electrochemical recycling of end-of-life scrap NdFeB magnets. By drawing ideas from different fields such as electrodeposition, selective dissolution, corrosion and also by projecting thermodynamic predictions for different rare earths of our interest, it can be observed that not only enhanced selective recovery of rare earths is possible but also it is, to an extent, a naturally favored process. The next step of this research will be to build up a 3-electrode electrochemical cell which can help establish the proof of concept described in the paper.
A more detailed look into the dissolution mechanism and kinetics of scrap magnets by using complimentary tools such as electroanalytical techniques and microscopy will be essential. Once the dissolution mechanism is understood, influence of different parameters such as pH, temperature, potential difference and electrolyte composition can be analyzed and optimized. The further goal will be to build up a lab scale cell which can handle few hundreds of grams of scrap in an efficient manner.

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PROPOSAL OF A NEW TYPE OF SULPHIDE ELECTROLYTE FOR RARE EARTH MOLTEN SALT ELECTROLYSIS

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Abstract

A new sulphide electrolyte is proposed for usage in rare earth molten salt electrolysis in the recycling of rare earths from magnet scrap. This electrolyte can be used at much lower temperatures and with much lower ecological impact than currently used chloride electrolytes in primary production in China. Most of the other properties of the electrolyte have yet to be determined. Most important aspects are the solubility of involved compounds, formation of anodic products, current efficiency and purity of rare earth metal product. The new technique is not only an important aspect in the recycling process of rare earths, but might also be implemented in primary production.

Introduction

The demand for rare earth metals has been increasing sharply since the year 2000. The most volatile rare earth products are currently rare earth magnets which contain a high amount of Neodymium besides smaller amounts of Praseodymium, Dysprosium and Terbium. Modern technologies like electric mobility or wind energy are highly depending on a reliable supply with rare earth magnets.

The difficulties with rare earth supply started with the rising demand for specific rare earth metals, like Neodymium for magnets. This situation led to a strong advance in prices for some rare earth metals while the less demanded metals became cheaper. Due to the composition of rare earth ores, an increase in production of specific rare earths is not possible, therefore the price gap became even greater.

Another problem is the monopoly position of China in rare earth supply with over 90 % of rare earths coming from China in the last years. In 2010, Chinese rare earth exports were restricted because of the demand on China’s own markets. Rare earth prices, in particular for the magnet metals, rose sharply in the rest of the world (Fig. 1).
After this incident, several countries dependent on rare earths started looking for alternative sources. In the US, Canada and Australia, new mining projects were founded and abandoned mines were reactivated. In Europe, no relevant primary production of rare earths is in place, mostly due to ecological requirements. Therefore, recycling is a promising and highly discussed source of rare earths in Europe. Since the beginning of 2013, there was a slight fall in rare earth prices, but still the high prices and the dependence on China as main supplier make recycling of rare earth magnets a possible successful alternative.

One key aspect in both primary winning and recycling of rare earth metals is the reduction of rare earth salt. For over a hundred years, molten salt electrolysis has been used for the reduction of nonprecious metals such as rare earths. Despite its old age, molten salt electrolysis has not advanced much, mostly due to difficult handling at high temperatures (>1000°C) and the resulting lack of scientific research. It is still possible to significantly improve molten salt electrolysis in terms of energy consumption and processability.
State of the Art

Existing molten salt electrolysis techniques are mainly chloride and oxy-fluoride electrolysis. The temperature in each case is often set to a higher value than the melting temperature of the desired rare earth metal, so the metal can be collected in a crucible below the cathode. These temperatures are between 800°C (Cerium) and up to 1700°C (Yttrium) respectively\(^14\). Alternatively, cathodes for formation of liquid alloys of cathode metal and rare earth or cathodes for solid precipitation can be used. The furnace chamber has to be flooded with inert gas, mostly argon, to prevent the reactive rare earth metals from corroding. Heating of industrial scale electrolysis baths is carried out by direct current, so no external heating system has to be used.

Chloride electrolysis uses rare earth chlorides in an eutectic mixture of sodium chloride and potassium chloride or other mixtures of alkaline chlorides. The cathode, either the bath container or a block electrode, consists of graphite, iron, or inert high-melting metals such as molybdenum. Chloride electrolysis is only reasonable below 1100°C, because the solubility of the product metal in the electrolyte increases significantly and the aggressive medium attacks the bath set-up\(^14\). The stability of rare earth metal in the electrolyte also influences the current efficiency which is relatively low at 45-50 %\(^14\). The chloride electrolysis produces Chlorine gas which is very toxic and corrosive. Despite its downsides, chloride electrolysis is used in rare earth production in China today.

In oxy-fluoride electrolysis a mixture of rare earth fluoride and oxide is dissolved in alkaline metal fluoride. Due to the high corrosiveness of fluoride components and the high temperatures, the bath may only contain graphite and refractory metal (e. g. molybdenum or tungsten) components. The better stability of high oxidation states in fluoride media has a positive effect on the current efficiency which is around 80 %. The anodic product is mainly carbon dioxide that is formed by the carbon electrode and oxygen from the melt. While not as harmful as chlorine, carbon dioxide emissions are controversially discussed because of climate change\(^15\). An even greater problem is the evolution of small amounts of extremely toxic and corrosive fluorine.

Latest trends in molten salt electrolysis research are highly concerned with higher energy efficiency and less ecological impact through waste products. An improvement in energy efficiency is reached by higher current efficiency of traditional processes\(^16\) and lower process temperature, e. g. through new electrolyte compositions\(^17\).

An interesting technique to reduce anodic exhaust gases is the use of sulphides in molten salt electrolysis to produce sulphur at the anode. The implementation of sulphides has been described in basic research, but not yet for rare earths. The production of aluminium from aluminium sulphide has been discussed\(^18\). Additionally, sulphides were used in the form of a
metal sulphide bulk material on the cathode. Tungsten and molybdenum have been won by this process on a laboratory scale\textsuperscript{19, 20}.

**Characteristics of molten salts**

Several important parameters of the electrolyte salt in molten salt electrolysis can be determined. The most obvious property is the melting point of the electrolyte, either of a single salt or a (eutectic) mixture. The melting point fixes the minimal possible temperature for the electrolysis. Normally, a temperature of about 100 K higher is necessary to reach a sufficient thermal movement of the melt and a sufficient diffusion of ions\textsuperscript{21}.

The electrolyte has a great contribution on the anodic product of electrolysis. It is dependent on available anions that can be oxidized on the anode. The anion can either come from the rare earth salt in the melt or the electrolyte salt. If more than one anion is used in the melt, the reacting one can be determined by the standard potential of the related redox pair. The anion with the highest potential is least likely to get reduced. Unfortunately, the electrode material and the deposition mechanism may affect the realistic potential of deposition, causing deposition at higher or lower potentials than the standard potential. These effects can be used advantageous for the process.

Solubility of rare earth salts and rare earth metals is also important. For the rare earth salt, a high solubility in the electrolyte is desirable. A greater amount of rare earth ion can be provided in the melt, resulting in a lower impact of diffusion on the electrodeposition\textsuperscript{22}.

**New Idea: Sulphide Electrolytes**

As mentioned above, sulphides have already been used as a bulk electrode to win Molybdenum, Tungsten and Sulphur. In this new concept, the sulphides are used as the main electrolyte, not a sulphide salt of the target metal, mostly because of the poor availability of rare earth sulphides and the hard soft acids bases theory (HSAB). Due to the necessary electrochemical stability, sulphide compounds of alkaline or alkaline earth metals are suitable. Unfortunately, those compounds have a melting point of at least 840°C (K₂S) therefore the use of lower melting polysulphides is planned (melting point K₂Sₓ: 471°C).\textsuperscript{24}

In the electrolysis process, the sulphide components will be oxidized to sulphur on a graphite anode. For the cathode, the use of the target rare earth metal is optimal for an easy post-processing. Also other electrode materials will be considered, like steel, nickel-base alloy or ceramic\textsuperscript{23}.
An important aspect in sulphide electrolysis is the collection of the won sulphur. With its boiling temperature at 444.6°C\textsuperscript{24}, the sulphur is expected to be gaseous at process conditions. The most reasonable solution would be to guide the sulphur through a heated pipe and condense it in a predefined separate container. Because of the difficulties in furnace geometry, this installation cannot be realised in short-term, so there will only be a hood at the anode for preventing the sulphur from distributing in the furnace chamber.

Experiments will be carried out in a retort furnace with a specially designed and insulated electrode feed-through. The conditions in the furnace chamber are temperatures up to 1100°C and inert atmosphere with nitrogen or argon gas. At first, only neodymium as the most important rare earth compound in magnets will be considered. Typical other rare earth metals in magnets are Praseodymium, Dysprosium and Terbium.

With the electrochemically active salt in the anodic reaction being the sulphide electrolyte, it is expected that several rare earth salts with more stable anions than sulphide can be processed in this kind of molten sulphide electrolysis. In rare earth processing, mainly oxides, chlorides, and fluorides occur which are all electrochemically more stable than sulphide. Additionally, rare earth sulphides are processible, although those salts do currently not play a role in rare earth treatment. A submitted project funded by BMBF will be dealing with the winning of Neodymium sulphides for recycling purposes. The plurality of usable Neodymium would be a great advantage of the sulphide electrolysis.

**Future Plans**

The next steps in validation of sulphide electrolytes for molten salt electrolysis have to be experimental testing of the postulated ideas. At first, we need to examine the basic properties
of alkali polysulfides concerning molten salt electrolysis, in particular melting temperature and general behaviour like vapour pressure and reactivity under electrolysis conditions.

As a key aspect, the solubility of affected chemicals, rare earth oxides, chlorides, and fluorides, will be quantified with high temperature potentiometric methods. As mentioned before, the solubility of Rare Earth salt has to be as high as possible for a sufficient supply with Rare Earth cations in the melt and a good current efficiency. On the other hand, the solubility of deposited metal in the melt has to be very low. If dissolved, the metal can migrate through the cell to the anode, get oxidized and start all over, significantly decreasing current efficiency. Additionally, the further treatment of the metal is much more difficult if it is dissolved.

Another very important aspect is electrochemical testing. Via cyclovoltammetry in a three electrode set-up, multiple reaction properties can be determined. At first, the potentials of the electrochemical reactions can be recognized at the points of highest current. Additionally, information about the reduction mechanism may be obtained, for example intermediate oxidation states of the products (RE$^{3+}$ → RE$^{2+}$ → RE$^{0}$) or surface reactions on the electrode$^{13}$. Another important outcome of electrochemical analysis is the theoretical yield of metal from the integration of the Faraday current over time.

The quality of electrodeposited rare earth metal is controlled by x-ray diffraction (XRD) and x-ray fluorescence analysis (RFA). In electrolysis, it is always possible to co-deposit other metals from the melt, even if their standard potential is significantly lower than the one of the desired metal. Additionally, the mass of won rare earth metal is important for comparison with theoretical yield for determination of current efficiency.

For validation of a possible industrial usage of our technique, scale-up is essential. With the current equipment, electrolysis with up to 10 l of electrolyte can be performed.

**Conclusions**

Sulphide electrolysis is considered a promising technique because of the possible low process temperature, a lack of exhaust gas, and lower voltage compared to state of the art oxide or chloride electrolysis. The technique can be used both in rare earth winning both from primary and secondary sources. Similar reactions have already been verified in laboratory scale in other fields.

A great effort in verifying the technique has still to be done, on laboratory scale as well as in scale-up. If the experiments lead to favourable results, sulphide electrolysis will become a serious alternative in electro-winning of non-precious metals.
References

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RARE EARTH EXTRACTION FROM NdFeB MAGNET AND RARE EARTH OXIDES USING MOLTEN SALT PROCESSES

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Abstract

In the present paper, the feasibility of the recovery of neodymium and dysprosium from spent Nd-Fe-B magnets (~6 wt% Dy) was investigated by using molten salt processes. The salt bath consisted of eutectic composition of NaCl-KCl-LiCl mixture. In order to enable an efficient dissolution of metal in the molten salt phase, AlCl3 was used as a chlorinating agent. Iron-free electrodeposition could be carried out successfully. EDS analysis of the electrodeposit revealed that co-deposition of the dysprosium occurs along with neodymium at the cathode. The process shows that this method is well-suited for recovering rare earth metals from magnetic scrap containing these metals.
Furthermore the set-up design for recovery of neodymium and dysprosium from their oxides, with regards to the previous studies on the neodymium magnets, was investigated. Stability of different fluorides and chlorides salts was studied by means of thermodynamic calculations. AlF3 based molten salt systems were studied in detail as the solvent in the rare earth oxide electrochemical extraction of Rare Earth Elements with Al.

Introduction

International concerns have been raised on the supply shortages of rare earth elements since China, the largest producer of rare earths, has reduced the export of these elements recently, while, on the other hand, global demand has increased over last years.
Neodymium magnets are used in different application such as hard disk drives, voice coil motors, magnetic resonance imaging sources because of their superior magnetic properties. Dysprosium is often used as additive element in neodymium magnets in order to keep the magnetic properties at high temperatures. An effective recovery method for Dy and Nd is needed, since almost all magnets are disposed after being used1.
Hydro-electrochemistry is not a feasible method for the recovery of rare earths since these elements have highly negative electrode potential and also they react with water and oxygen. Therefore, molten salt solutions are selected for electrowinning of rare earths2. In this work
we have used molten salt chloride in order to electro-reduce the rare earth elements from their magnet.

The other important issue which has been discussed in the recent years among the researchers is the recovery of rare earths from rare earth oxides (REO). Different methods were used in order to remove the oxygen from rare earth oxides: direct electrochemical deoxidation process, solid state electrotransport (SSE), oxyhalide formation and calcium-halide deoxydation which was further combined with electrolysis in order to balance the CaO activity in the molten salt. Yet the strong affinity of rare earth metals to oxygen has made it difficult to industrialize any of these methods except molten salt electrolysis.

In this paper we will discuss the possibility of using aluminium chloride as the Nd (and Dy) chlorination agent for NdFeB magnets, and using aluminium fluoride as a strong fluxing agent in the molten fluoride to react with rare earth oxide and form rare earth fluoride which can be further subjected to electrolysis under the applied voltage.

**Thermodynamic considerations**

**NdFeB magnets containing Dy**

Efficient dissolution of metal in the molten salts depends on the choice of fluxing agent. Earlier works on the extraction of Fe, Cr and Nd from industrial electric arc furnace slag (EAF), chromite ore and spent neodymium magnets respectively, have proven that AlCl3 can act as a powerful chlorinating agent. The reaction between the magnets and AlCl3 leads to the metal chloride formation. The formed metal chloride will be subjected to the electrolysis and will be reduced on the cathode.

The standard Gibbs energy for different metal chlorides formation (metals present in the magnets), using AlCl3 as the chlorinating agent, was calculated by using the FactSage software (FactSage 6.3). The results show that the Nd and Dy trichlorides are more stable than AlCl3, while the formations of FeCl3, FeCl2 and BCl3 are not favoured. The Gibbs energies of the corresponding reactions are listed in table 1.

**Table 1: Gibbs energy values of the reaction of AlCl3 with the different metals in the system.**

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl3(salt)+Dy(s)=DyCl3+Al(liq.)</td>
<td>-206.2</td>
<td>-353.5</td>
<td>-291.2</td>
<td>-293.9</td>
</tr>
<tr>
<td>AlCl3(salt)+Nd(s)=NdCl3+Al(liq.)</td>
<td>-247.8</td>
<td>-368</td>
<td>-331.4</td>
<td>-330.2</td>
</tr>
<tr>
<td>AlCl3(salt)+Fe(s)=FeCl3+Al(liq.)</td>
<td>296.7</td>
<td>337.7</td>
<td>296.4</td>
<td>306.6</td>
</tr>
<tr>
<td>AlCl3(salt)+1.5Fe(s)=1.5FeCl2+Al(liq.)</td>
<td>207</td>
<td>165.1</td>
<td>176.8</td>
<td>193.2</td>
</tr>
<tr>
<td>AlCl3(salt)+B(s)=BCl3+Al(liq.)</td>
<td>180.2</td>
<td>195.3</td>
<td>242.4</td>
<td>303</td>
</tr>
</tbody>
</table>

From these results it can be concluded that Nd and Dy react with AlCl3 and as a result, NdCl3 and DyCl3 are formed in the salt bath. It should be noted that these calculations are based on
the pure substances at their standard state at 1073 K, whereas the activity of Nd and Dy in the magnet as well as the activity of the chlorides would change after the dissolution in the salt bath. The formed rare earth chloride will be decomposed according to the reaction (1):

\[ \text{RECl}_3 = \text{RE}^{3+} + 3\text{Cl}^- \]  \hspace{1cm} (1)

The decomposition voltage of the different metal chlorides and alkali chlorides were calculated using FactSage software and the results are presented in Figure 1.

![Figure 1](image)

**Figure 1:** Calculated decomposition voltage as a function of temperature for the chlorides formed in LiCl–KCl–NaCl–AlCl₃ molten salt bath.

An overpotential of 0.8 V was suggested for the decomposition of NdCl₃ in the earlier work. Considering that Nd and Dy possess similar properties and also based on the decomposition voltage of DyCl₃ shown in Figure 1 (2.6 V at 800°C), a voltage of 3.4 V was applied for the electrode decomposition of DyCl₃.

**Electrochemical reduction of rare earth oxides**

For the electrochemical reduction of REOs, the first step is the electrolyte selection. The reduction potential of the solvent should be more negative than the reduction potential of the rare earth oxides, meaning that the solvent has to be more stable than the solute. In order to compare the stability of different chloride and fluoride solvents, thermodynamic studies were performed on the solvent components as well as the oxides. The Gibbs energy formations of the rare earth oxides and the most common molten salts, calculated using FactSage, are listed in Table 2.
Table 2: Gibbs energy values of the decomposition of different salts and oxides in the system

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG(kJ/mol) at 850° C</th>
<th>Decomposition potential(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd₂O₃(s) = 2Nd(s)+3/2 O₂(g)</td>
<td>1491.7</td>
<td>-2.5</td>
</tr>
<tr>
<td>Dy₂O₃(s) = 2Dy(s)+ 3/2 O₂(g)</td>
<td>1534.9</td>
<td>-2.6</td>
</tr>
<tr>
<td>NdF₃(s)=Nd(s) + 1.5 F₂(g)</td>
<td>1392.6</td>
<td>-4.8</td>
</tr>
<tr>
<td>DyF₃(s)=Dy(s) + 1.5 F₂(g)</td>
<td>1414.5</td>
<td>-4.8</td>
</tr>
<tr>
<td>CaF₂=Ca + F₂</td>
<td>1036.8</td>
<td>-5.3</td>
</tr>
<tr>
<td>LiF = Li + 0.5F₂</td>
<td>504.6</td>
<td>-5.2</td>
</tr>
<tr>
<td>NaF= Na + 0.5 F₂</td>
<td>468.3</td>
<td>-4.8</td>
</tr>
<tr>
<td>KF= K + 0.5 F₂</td>
<td>459.3</td>
<td>-4.7</td>
</tr>
<tr>
<td>CaCl₂= Ca + Cl₂</td>
<td>625.8</td>
<td>-3.2</td>
</tr>
<tr>
<td>LiCl= Li + 0.5 Cl₂</td>
<td>322.8</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

From the thermodynamic results, it can be seen that between CaF₂, LiF, KF and NaF at 850° C, the most stable fluoride is CaF₂. Hence the relative stability of these metal fluorides is: CaF₂>LiF>NaF>KF. Comparing the decomposition voltage of rare earth fluorides and the alkali fluorides and chlorides, it can be seen that only CaF₂ and LiF are more stable than NdF₃ and DyF₃. In other words, in the case of using NaF, KF, CaCl₂ and LiCl, we can expect that Na, K, Ca and Li (respectively) will be reduced on the cathode before the reduction of rare earths. Therefore, for the electrochemical deposition of rare earth oxides, the most suitable solvents among fluorides are CaF₂ and LiF. Considering the high melting point of calcium fluoride (1418°C), the eutectic composition of LiF-CaF₂ (79-21 mol%, shown in Figure 2), is a suitable option to be used as the molten salt solvent for the electrochemical reduction of the rare earth oxides.
The experimental results of Hamel et al.\textsuperscript{12} support the thermodynamic results in the present study. These authors have measured the standard potential of different fluorides solvent in order to find the most suitable solvent for reduction of Nd. Their results show that in LiF-NaF and LiF-KF systems, no electrochemical reduction of Nd is observed.

Comparing the relative advantages of AlF\textsubscript{3} and AlCl\textsubscript{3} for electrochemical reduction of Nd and Dy from Nd magnets, trials with AlCl\textsubscript{3} indicated the loss of some of the aluminium chloride added to the vapour phase from the molten chloride bath before getting dissolved in the molten salt due to the high vapour pressure\textsuperscript{11}. AlF\textsubscript{3} on the other hand, was found in the present work as a suitable reduction agent candidate for the electrolysis of rare earth oxides in molten fluorides. From the calculated Gibbs energy of the reaction,

\[ Nd_2O_3 + 2AlF_3 = Al_2O_3 + 2NdF_3 \quad \Delta G(T = 850^\circ C) = -177.7 \text{ kJ mol}^{-1} \] (2)

it is seen that aluminium fluoride can react with rare earth oxides forming rare earth fluorides, which can be further reduced at the cathode. In-situ formation of REF\textsubscript{3} is very important since the solubility of REOs is very low in the molten fluorides. Stefanidaki et al.\textsuperscript{13} have studied the oxide solubility and Raman spectra of Nd\textsubscript{2}O\textsubscript{3} in the alkali fluorides. They have reported that the NdF\textsubscript{3}\textsuperscript{3-} anion is the dominant complex in the eutectic NdF\textsubscript{3}-LiF melt system and when Nd\textsubscript{2}O\textsubscript{3} is added, NdOF\textsubscript{5}\textsuperscript{6-} complex might form in the melt. They have found that the solubility of Nd\textsubscript{2}O\textsubscript{3} varies from 0.15-0.38 mol\% when the NdF\textsubscript{3} concentration changes from 15-30 mol\% at 900\textdegree C. This is in support of the earlier results that M\textsubscript{x}O\textsubscript{y} oxide solubility in electrolyte is enhanced with the MF\textsubscript{x} salt\textsuperscript{13}. Another important advantage of in-situ formation of REF\textsubscript{3} as
the result of reaction of REO with aluminium fluoride is that the formation of rare earth oxyfluoride might be prohibited.

Contradictory results have been reported on the electrochemical reduction of rare earth oxyfluorides in the molten salts, which shows that further investigation is needed. According to Taxil et al.14, Ln fluorides in the presence of the metal oxides will form rare earth oxyfluoride which is an insoluble product. Stefanidaki et al.15 have shown that the neodymium oxyfluoride is not reduced to neodymium metal. In the voltammetric characterization of LiF-NdF3-Nd2O3 system, they have observed the same voltammogram as the one for LiF-NdF3 system. They have concluded that neodymium is reduced on the tungsten cathode by electroreduction of neodymium fluorides (present in the form of [NdF6]3–), while oxygen is generated on the glassy carbon anode by oxidation of neodymium oxyfluorides (present in the form of [NdOF5]4–), producing CO and CO2 gasses15. They believed that electrochemical production of neodymium in an oxyfluoride melt is possible at low voltage electrolysis, in which fluoro-carbon compounds are not formed. Thudum et al.16 have shown that neodymium in LiF-CaF2-NdF3-Nd2O3 and LiF-CaF2-LaF3-Nd2O3 systems can be reduced both from neodymium oxyfluorides and neodymium fluoride ions, depending on the neodymium oxyfluorides to neodymium fluoride ions (OF/F) molar ratio. At low OF/F, [NdF6]3– are reduced to neodymium. Meanwhile above a critical Nd2O3 concentration, [NdOF3]4– are cathodically active ions and are reduced on the cathode. Kaneto et al.17 have suggested that in the oxyfluoride system, oxygen is generated on the anode, while fluorine can be produced at the anode at higher cell voltage.

As it was discussed earlier, in-situ formation of AlF3 might reduce the problem of low solubility of REOs in molten fluorides.

**Experiments for electrochemical reduction of Dy and Nd from NdFeB magnets containing Dy**

The ternary eutectic composition of LiCl-KCl-NaCl salt (55 mol-% LiCl, 35 mol-% KCl and 10 mol-% NaCl) was dried at 473 K for at least 24 hours. High purity aluminium chloride (99%) was added as the fluxing agent. Neodymium magnets containing approximately 6 wt% dysprosium were crushed into small particles and were used as Dy source. According to the results from scanning electron microscopy (SEM) equipped with an energy dispersive spectroscopy probe (EDS) analysis, chemical composition of the magnet was indicated as Fe14Nd1.4Dy0.6 (boron, being a light element could not be detected in EDS analysis).

Experiments on reduction of Nd and Dy from scrap magnets in molten chlorides were performed at temperature 1073 K for 6 hours. The flux/neodymium and flux/salt ratio were chosen as 2 (molar fraction) and 20 (wt%) respectively. Table 3 shows the amounts of different components used in the experiments.


Table 3. Amounts of different components used in the electrolysis experiment (wt%)

<table>
<thead>
<tr>
<th>Composition</th>
<th>AlCl₃</th>
<th>Nd₂Fe₁₄B</th>
<th>NaCl</th>
<th>KCl</th>
<th>LiCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(wt%)</td>
<td>3.14</td>
<td>9.18</td>
<td>1.59</td>
<td>7.48</td>
<td>6.63</td>
</tr>
</tbody>
</table>

Salt mixture, flux and magnets were heated up to 1073 K in an alumina crucible in a vertical furnace. Inert atmosphere containing argon gas was used which was dehydrated by passing through silica gel. Graphite rods were chosen as anode and cathode in view of their additional advantage as oxygen getters. The electrolysis was started by dipping the electrodes into the salt bath and a constant voltage of 3.4 V was applied by a DC power supply (HP, Hewlett, 6632A) based on the decomposition voltage of the DyCl₃ at 1073 K. Figure 3 shows the schematic diagram of the set-up. After 6 hours electrolysis, the crucible was cooled down under the argon gas. The deposited layer on the graphite cathode was separated and washed with distilled water in order to dissolve the salts. After removing the salts, the deposited powder was dried and prepared for the analysis. To investigate the morphology and composition of the deposited product, SEM/EDS analysis was carried out.

![Figure 3](image)

**Figure 3.** (a) Schematic diagram of the set-up (b) Image taken from graphite cathode after electrolysis at 1073 K for 6 hours in argon atmosphere.

**Results**

The microstructures of the cathode samples were analyzed by SEM and are presented in Figure 4. The phase with bright contrast in this image, indicated by A was confirmed to be a metallic phase consisting mostly of dysprosium and neodymium. The phase with dark contrast indicated by B is aluminium oxide phase. The composition of the metallic phase on cathode samples, analyzed by EDS is presented in Figure 5. The data from EDS point analysis show presence of neodymium and dysprosium in the deposited product which is dominant.
in comparison to other elements. It should be noted that oxygen detection with EDS is not reliable.

Figure 4. SEM image of cathode deposition after electrolysis of magnet, using AlCl₃ as flux, at V=3.4 V and T=1073 K during 6 hours. A is the metallic phase (Dy-Nd), B is the oxide phase.

Figure 5. EDS pattern of Dy-Nd deposit on graphite cathode in LiCl-KCl-NaCl molten salt at 1073 K.

The formation of Dy-Nd metallic phase on the cathode was also investigated by EDS mapping analysis of the sample, shown in Figure 6. The intensity of the colour in the image related to neodymium is very low, however it can be seen that dysprosium and neodymium are distributed in the same areas, confirming the formation of metallic phase, since these regions are poor in oxygen. It can be also seen that aluminium and oxygen are distributed in the same areas which shows the formation of aluminium oxide phase. Dysprosium deposition along with neodymium was confirmed using molten salt electro-deposition method.
Figure 6. Mapping images of Dy-Nd-Al-O deposit on graphite electrode in LiCl-KCl-NaCl molten salt at 1073 K.

It was not possible to detect boron in the EDS analysis due to it being a light element. In the earlier studies on the electrochemical reduction of neodymium from Nd magnet scraps, the results from wavelength dispersive spectroscopy (WDS) showed that boron remains in the bulk salt bath, and the intensity of the boron peak in the cathode sample was lower than the detection limit, shown in figure 7.

Figure 7. Intensity scan over the boron peak position in the salt bath sample and cathode sample from the earlier study.
Discussion

The eutectic composition of LiCl-NaCl-KCl ternary mixture was used as electrolyte for the electrochemical decomposition of NdFeB magnets containing dysprosium. Aluminium chloride was used as the fluxing agent. It is proven in different studies\textsuperscript{19,20} that aluminium chlorides exist in the form of AlCl\textsuperscript{4} ionic species in the alkali chlorides solvents, which results in the formation of a pseudo–binary solution.

The results from SEM/EDS show the presence of Nd-Dy metallic phase in the deposited material. This is explained by the proximity of their electrode potentials. It can be concluded that neodymium and dysprosium have been dissolved in the alkali chloride melt, forming RECl\textsubscript{3}. In fact, the results from Raman spectrometry have confirmed that neodymium(III) exists as NdCl\textsubscript{3}\textsuperscript{−} complex with octahedral symmetry in the molten alkali chlorides\textsuperscript{21}. Thus, in the chloride melt, the rare earth elements dissolve according to\textsuperscript{22}:

\[ RE(III) + 6Cl^- = RECl_6^{3-} \quad (3) \]

Considering the cathodic and anodic electrochemical reactions, these can be represented as:

Anodic reaction \[ 3Cl^- = \frac{3}{2} Cl_2 + 3e^- \quad (4) \]

Cathodic reactions \[ Nd^{3+} + 3e^- = Nd \]
\[ Dy^{3+} + 3e^- = Dy \quad (5) \]

RE\textsuperscript{3+} is the most stable state of the rare earth metals in the molten salts\textsuperscript{23}. It has been reported that most of the rare earth elements (La, Ce, Pr, Y) have a single decomposition signal in the molten chlorides, however Nd reduction occurs in two steps\textsuperscript{22}. The formation of divalent rare earth metal ions in the chlorides melt is most likely to be one of the reasons for decreasing the current efficiency, which would be caused by two-step reduction of the rare earth metals:

\[ RE^{3+} + e^- = RE^{2+} \quad (6) \]
\[ RE^{2+} + 2e^- = RE \quad (7) \]

Contradictory results have been reported on the electrochemical mechanism of neodymium and dysprosium reduction in molten salts. It has been reported that the reduction process of NdCl\textsubscript{3} to Nd metal in pure chloride\textsuperscript{24}, LiF–CaCl\textsubscript{2} melts\textsuperscript{25}, LiF–CaF\textsubscript{2} and LiCl–KCl\textsuperscript{27} is a one-step mechanism. However, De Córdoba et al.\textsuperscript{28} and Masset et al.\textsuperscript{29} have confirmed that the reduction of NdCl\textsubscript{3} takes place in two steps.

Electrode material is one of the factors that can influence the electrochemical reduction behaviour of the rare earths in molten salts. Castrillejo et al.\textsuperscript{30} have observed that their cyclic voltammogram results exhibit different behaviours of dysprosium on the W and Al
They have observed that, on the W electrode, Dy is reduced in two steps, viz. Dy(III) → Dy(II) → Dy(0), while on the Al electrode the electrochemical reaction would be:

\[ \text{Dy(III)} + 3\text{Al} + 3e^- = \text{DyAl}_3 \]  

(8)

In order to get a clarification of the electrochemical mechanism of rare earth reduction in the molten salts, further studies are required.

The study of the electrochemical reduction of Nd and Dy from neodymium magnets containing dysprosium is based on a new process line for the electrolytic recovery of rare earths, which can be shown as the flow chart in Figure 8.

**Conclusion**

Feasibility of the neodymium and dysprosium extraction from Nd$_2$Fe$_{14}$B magnets containing 6% dysprosium was investigated using the molten salt method. In the present approach it was shown that neodymium and dysprosium recovery from magnetic scrap enables a direct separation of these metals from iron, eliminating the oxide or halide conversion steps. Simplicity of this method due to the single step recovery of the RE metals from the magnet scrap, makes this process attractive from the industrial point of view. Compared to hydrometallurgical approaches, this process has advantage of being more environmentally-friendly since the salt bath can be reutilized without contaminating the environment.

Further, based on thermodynamic calculations, it was shown that strong tendency for AlF$_3$ towards reaction with Nd$_2$O$_3$ and Dy$_2$O$_3$ would enhance the in-situ formation of rare earth fluorides in the salt bath and thereby increase the solubility of REOs in the molten fluorides. Hence AlF$_3$ can act as a powerful flux agent in the fluorides melt for recovery of rare earth

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Figure 8. Schematic diagram of the salt extraction process
metals from their oxides. The use of AlF₃ will be experimentally explored in the forthcoming studies.

**Acknowledgements**

Part of this work that is related to rare earth extraction from scrap magnet was carried out in Royal Institute of Technology (KTH) in Sweden and was supported by Swedish Foundation for Strategic Environmental Research (MISTRA) through Swedish Steel Producers Association (Jernkontorets). We are also grateful to the EU-FP7 project of “EREAN” (Project ID 607411) for the financial support on the reduction of rare earth from rare earth oxides.

**References**

Session V-A: REE Processing- Mineral Beneficiation / Leaching
RECOVERY OF RARE EARTH ELEMENTS FROM CLAY MINERALS

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Abstract

Continuous development of advanced technologies has created increasing demand for rare earths elements (REE), with global emphasis on identifying new alternate sources to ensure adequate supply. Clay deposits containing physically adsorbed lanthanides are substantially lower grade than other types of REE mineral resources; however, their abundance in sub-tropical regions, existence as surface layers requiring low mining cost, and their high cation exchange capacity make them economically-important sources of rare earths. At the University of Toronto we have conducted a systematic study of clay minerals from various locations. It was found that REE are easily recovered via an ion-exchange mechanism during leaching with monovalent salt solutions under ambient conditions, based on a 3:1 stoichiometric ratio between the trivalent lanthanides and the exchange monovalent cation. The present paper reports on the most important findings of this investigation.

I. Background

Rare earths, also known as lanthanides, are a series of 17 elements with unique properties that make them essential for the hi-tech industry because of their various uses in high strength permanent magnets, lasers, automotive catalytic converters, fiber optics/superconductors, and electronic devices. They are grouped depending on the atomic number, in “light” rare earth elements (REE)—La, Ce, Pr, Nd, and “middle & heavy” REE—Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y. Because of the ongoing development of new advanced technologies, there is an ever-increasing demand for lanthanides in the international markets, with emphasis on identifying new resources to ensure adequate supply for present and future use. World production of REE is dominated by China, the United States and Australia; however, in terms of reserves and resources, China dominates the world potential with reserves estimated to be around 50% of the total while completely leading and controlling the global production at ~ 90%.¹ For the last 3 decades, R&D in the field of REE in most of the Western world has slowed down due to the import of these elements from China. Consequently, the development of specialized extraction, refining and processing technologies, including equipment and training of
engineering expertise were allowed to lapse, creating thus a dependence on Chinese supplies. Starting with 2005 China – the undisputed leader in both REE innovation and trade, has been restricting yearly export quotas for REE ores in order to have enough resources for its own industries and to gain control over the global market, especially for the heavy and scarcer rare earths. Consequently, the last decade has brought a renewed concerted global drive towards REE research and development, led by USA and Japan, with the dual scope of finding new resources and improving processing/extraction technologies, as summarized by Adachi, Imanaka and Tamura.

REE are part of many various rock-forming minerals, but the most commercially significant sources, as reviewed by Kanazawa and Kamitani, fall into the following categories:

1) **Bastnasite**, \((\text{REE, Ce})(\text{CO}_3)\text{F}\), is a magma-derived fluorocarbonate mineral containing 65-75 \%wt. light rare earth oxides (REO) and accounts for more than 80\% of global REO production. The two major sources in the world for lanthanides are bastnasite deposits at Mountain Pass, California (U.S.A) – devoted solely to REE production, and Bayun-Obo, Inner Mongolia (China) – mined primarily for iron ore and REE as by-product.

2) **Monazite**, \((\text{REE})\text{PO}_4\) is a light REE phosphate containing 55-65 \%wt. REO, associated with granites and beach sands in Australia, Brazil and India. Until about 1965 monazite was the main REE source; since then, the use of monazite has been considerably reduced due to radioactivity caused by thorium and radium.

3) **Xenotime** \((\text{Y,REE})\text{PO}_4\) is an yttrium-rich phosphate containing 25-60 \%wt. \(\text{Y}_2\text{O}_3\) and other heavy REE. It is mainly recovered as by-product of mining for titanium, zirconium and tin in Malaysia, Indonesia and Thailand.

4) **Weathered Crust Elution-deposited Rare Earth Ores** (common name: Ion-adsorption Clays) are aluminosilicate minerals (e.g. kaolinite, illite, and smectite) containing 0.05-0.3\% \%wt. REEs are physically adsorbed at sites of permanent negative charge. The ion-adsorption clay deposits are the result of in-situ lateritic weathering of rare-earth rich host rocks (granitic or igneous), which lead over geological times to the formation of aluminosilicate clays. These very fine mineral particles have the capability of adsorbing lanthanide ions released/dissolved during weathering. Sub-tropical climates present ideal conditions for this lateritic process to occur. The best example of this formation process exists in Southern China (latitudes 24-26°N), where many of such deposits are known to exist, as described by Bao and Zhao. In spite of their low grade, ion-adsorption clays account for ~ 35\% of the China’s total REE production, according to Yang et al.

Carbonate and phosphate sources, in spite of being high grade, are associated with elevated recovery costs due to difficulty in mining, separation, beneficitation and need of aggressive conditions to dissolve the REE. For example, bastnasite is generally leached with concentrated \(\text{H}_2\text{SO}_4\) or \(\text{HCl}\), whereas monazite/xenotime concentrates need to be baked either in 98\% \(\text{H}_2\text{SO}_4\) or 70\% \(\text{NaOH}\) to render REE soluble. Secondary REE sources
include apatite and the so-called “hard-rock” deposits such as zircon, titanate, niobate, allanite, eudialyte, gadolinite, but these contain less than 30% REE and require even harsher conditions for breaking down the mineral matrix (e.g. caustic bake followed by acid leaching); the processing of these ores is mainly directed towards extraction of niobium, tantalum and zirconium.  

Although ion-adsorption clay deposits are substantially lower grade than other types of lanthanide sources, the lower grade is largely offset by the easier mining and processing, costs, and the very low content of radioactive elements (normally associated with yttrium). These deposits are mined by open-pit methods and no ore beneficiation is required. A simple leach using monovalent sulphate or chloride salt solutions at ambient temperature can produce a high-grade REO product. Because of their abundance in surface layers in nature, ease of mining and processing, these clays warrant a detailed study as important sources of rare earths.

II. Formation of Weathered Crust Elution-deposited Rare Earth Ores (Ion-adsorption Clays)

The ion adsorption clay deposits of REE were first discovered in 1969 in the Jinangxi province (southern China) and declared a novel type of exogenous rare earth ore. Since then, more deposits were discovered and mined all throughout the South of China, as indicated by Figure 1.

![Figure 1: Locations of REE-bearing ion-adsorption clay ores in China](image)

The formation of this type of ore is due to physical, chemical and biological (microbial) weathering of REE-rich granitic and volcanic rocks under warm, humid, slightly acidic
conditions in subtropical zones. According to Bao and Zhao,\(^5\) the weathering crusts are up to 30 m deep and divided into four layers: (A) An upper humic layer of quartz, organic matter and soil: 0–2 m thick, with very low/nil REE content; (B) a strongly weathered layer enriched in REE: 5–10 m thick with kaolinite, halloysite, quartz and mica; (C) a semi-weathered layer: 3–5m thick with kaolinite and sericite; (D) a weakly weathered bottom layer with the same mineral compositions as the host rock. 80-90% of the adsorbed REE report to the strongly weathered layer (B) whereas less than 15% are found in the semi-weathered later (C). Depending obviously on the nature of the original host rocks, the general components of the weathered ores are kaolinite, halloysite and mica, with a typical composition (as %wt.) of ~70% SiO\(_2\), 15% Al\(_2\)O\(_3\), 3-5% K\(_2\)O, 2-3% Fe\(_2\)O\(_3\) and less than 0.5% of CaO, MgO and other elements.\(^8\) The metallogenic mechanism of formation for the weathered REE deposits, as proposed by Peng\(^11\) and later expanded by Hendrick\(^12\) is presented in Figure 2.

Considering the geological and climate conditions for the formation of REE-bearing weathered ores, there is no reason to limit the occurrence of this type of deposits within Chinese borders. While at the present time China is the only country to actively pursue and develop this type of resource to commercially produce REE, recent geological surveys (summarized by Chen\(^13\)) have led to the discovery and investigation of similar ion adsorption clay deposits in South America\(^14\) and Africa,\(^15\) located in the same subtropical weathering areas as depicted in Figure 3.

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**Figure 2:** Metallogenic mechanism of formation for REE-rich adsorption-type ores (adapted from Peng\(^11\) and Hendrick\(^12\))

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III. Nature of Rare Earth Elements in Ion-adsorption Clays

Clay minerals are part of the phyllosilicate class, containing layered structures of shared octahedral aluminum and tetrahedral silicon sheets; water molecules and hydrated cations can move in and out of the interlayer spaces. Very often, isomorphous substitution of one cation with another (of similar size but with lesser charge, e.g. Al$^{3+}$ for Si$^{4+}$ or Mg$^{2+}$ for Al$^{3+}$) within crystal structures leads to a charge imbalance in silicate clays, which accounts for the permanent negative charge on clay particles, thus the ability of clays to attract cations to the surface. Amphoteric -OH groups at the surface/edge of clays (i.e., silanol and aluminol) may also contribute to surface charge (pH-dependent reversible charge).\textsuperscript{16}

According to Bradbury and Baeyens\textsuperscript{17} as well as Piasecki and Sverjensky,\textsuperscript{18} for acidic and near-neutral conditions (pH < 6.5-6.8), most of the surface-adsorbed lanthanides occur as simple or hydrated cations such as “clay-REE” or “clay-REE(H_2O)_n” species derived from straightforward cation-exchange reversible reactions at the permanent negative charge sites on the clays (physisorption); for pH > 7 the prevalent form is the hydrolyzed “clay-O-REE$^{2+}$” species derived from permanent complexation reactions at the amphoteric surface hydroxyl groups (chemisorption) or soluble carbonate/bicarbonate complexes.\textsuperscript{8}
Due to various weathering conditions (i.e. nature of host rocks, water and soil pH, temperature, pressure, redox conditions) there are three main categories of REE present in the ion-adsorption clays, as described by Chi and Tian:

1. **Colloid phase**: REE deposited as insoluble oxides or hydroxides or as part of colloidal polymeric organometallic compounds. These species have low occurrence in ores at the slightly acidic natural conditions and can be recovered only by acid leach.

2. **Exchangeable phase**: REE occur as soluble free cations/hydrated cations or part of positively-charged complexes in solution adsorbed species on clays. These species account for 60-90% of total content of rare earths in ores and can be recovered by ion-exchange leaching with monovalent salts.

3. **Mineral phase**: REE part of solid fine particles with same mineral matrix as the host rocks (REE part of the crystal lattice). This phase usually accounts for the balance from the ion-exchangeable phase towards the TREE content and can be recovered only by aggressive conditions (alkaline bake and acid leach).

The vast majority of the ion-adsorption ores present the “negative cerium anomaly”, meaning that, contrary to the majority of lanthanide elements which are usually physically adsorbed as trivalent ions, Ce$^{3+}$ can be easily oxidized by atmospheric oxygen (O$_2$) to Ce$^{4+}$, and precipitates as cerianite, CeO$_2$. Consequently, the formation of the mineral cerianite facilitates a natural separation of Ce from the other adsorbed trivalent lanthanides, as described by Bao and Zhao, and makes it impossible to be recovered by ion-exchange leaching.

Depending on the nature of the original host rocks, other metals will get dissolved and carried downstream during the weathering, decomposition and alteration processes. The main impurities associated with the ion-adsorption ores are usually Al, Mg, Ca, Mn, Zn and Fe. While most base metals occur as part of the mixed mineral phase and do not leach out during the mild ion-exchange REE leaching conditions, Al especially and to a lesser extent Ca and Mg constitute the major impurities physically adsorbed on clays that are liable to get desorbed during the process along with the lanthanides.

**IV. Overview of Leaching Technologies for the Ion-Adsorption Clays**

As previously described, the ion-adsorption clays contain anywhere between 0.05 to 0.3 wt.% rare earths, out of which 60-90% occur as physically adsorbed species recoverable by simple ion-exchange leaching. In the typical procedure, the ores are leached with concentrated inorganic salt solutions of monovalent cations. During leaching, the physisorbed REE are relatively easily and selectively desorbed and substituted on the substrate by the monovalent ions and transfer into solution as soluble sulphates or...
chlorides, following a 3:1 stoichiometry (Eqn. 1). Solubilized REE are usually selectively precipitated with oxalic acid to form oxalates (Eqn. 2) that are subsequently converted to REO via roasting at 900 °C according to Eqn. 3. Finally, the mixed REO are separated into individual REE by dissolution in HCl and fractional solvent extraction.

\[
\begin{align*}
2 \text{Clay-REE} + 3 \text{M}_2\text{SO}_4 & \rightarrow 2 \text{Clay-}\text{M}_3 + \text{REE}_2(\text{SO}_4)_3 \quad (1) \\
\text{REE}_2(\text{SO}_4)_3 + 3 \text{H}_2\text{C}_2\text{O}_4 + 10 \text{H}_2\text{O} & \rightarrow \text{REE}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \quad (2) \\
\text{REE}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O} & \rightarrow \text{REE}_2\text{O}_3 + 3\text{CO} + 3\text{CO}_2 + 10\text{H}_2\text{O} \quad (3)
\end{align*}
\]

Various research conducted on the desorption of REE from clays via ion-exchange leaching\(^8,9,10\) indicated that, regardless of the initial content, not all REE reached similar extraction levels. Coppin et al.\(^20\) reported that the amount of trivalent lanthanide ions adsorbed on smectite and kaolinite was inversely proportional to the ionic radii and pointed to a fractionation during selective sorption of lanthanides, with heavy elements (i.e., higher atomic number: Tb to Lu) being adsorbed stronger than the light ones (i.e., La to Gd). They related this behavior to the “lanthanide contraction” in the ionic radii going from light to heavy REE. Based on these observations, it was inferred that desorption must exhibit a similar trend, with heavy REE being more difficult to extract, probably according the trend

\[
\text{Sc} > \text{La} > \text{Ce} > \text{Pr} > \text{Nd} > \text{Sm} > \text{Eu} > \text{Gd} > \text{Tb} > \text{Dy} > \text{Ho} > \text{Y} > \text{Er} > \text{Tm} > \text{Yb} > \text{Lu}
\]

Ever since the discovery of the weathered crust elution-deposited rare earth ores in the Jingxi province about 45 years ago, China was at the forefront of research and development of this kind of unique deposits, applying the ion-exchange leaching procedure for the extraction of lanthanides via three successive generations of technology, as summarized by Chi and al.\(^21\) and presented below.

**The first generation leaching technology – batch leaching with NaCl**

In the early 1970s, the ores were processed by opencast mining, sieved and leached with ~1M NaCl in barrels, followed by oxalic acid precipitation. The main disadvantages of this initial approach were small scale, low yields, high lixiviant concentration needed and poor product quality (<70% TREO content due to Na oxalate coprecipitation), which greatly surpassed the advantages of extremely low costs and fast processing times. By mid-1970s the procedure was changed to bath leaching in concrete pools in order to increase production; however, the main disadvantage of low product purity remained and, because of the largely unregulated and illegal/clandestine mining and extraction practices, the environmental impact was devastating, including severe loss of vegetation and biodiversity, soil erosion and water contamination (both streams and phreatic).
The second-generation leaching technology – batch and heap leaching with \((\text{NH}_4)_2\text{SO}_4\)

In the early 1980s, 1M NaCl was replaced by ~ 0.3M \((\text{NH}_4)_2\text{SO}_4\) as lixiviant for batch leaching, which required less reagent consumption due to increased desorption capabilities of \(\text{NH}_4^+\) as compared to \(\text{Na}^+\) and led to improved final product purity (> 92% TREO content). The procedure was so successful that it became the primary leaching method for the next approximately 20 years and largely contributed to the intense development of REE ion-adsorption research. However, the second-generation batch leaching technology led to environmental impact as well, due to mining-related deforestation and discharge of tailings and was ultimately replaced in early 1990s by the heap leaching procedure.

In the traditional heap leaching procedure, the soil pile (1.5-5 m high) is built on a flat impermeable (leak-proof) layer 5-20 cm thick inside a cofferdam ~ 50 cm high as to prevent solution overflow. The lixiviant is injected into the top of the pile at a solid to liquid (S:L) ratio of ~0.25:1 and accumulates at the bottom in the collecting ditch. Washing is performed with clean water at a S:L ratio of ~0.6:1; depending on the size of the ore heap, leaching time ranges from 100 to 320 hours and REE extraction can reach up to 90%. This procedure is very well suited for the processing of very low-grade ores.
The third-generation leaching technology – in-situ leaching with (NH₄)₂SO₄

The intense and largely unregulated use of successful batch and heap leaching with ammonium sulphate for ~2 decades led to severe and long-lasting environmental, ecological and health damages in southern China; as an example based on Yang’s paper, by 2010 the REE mining in Guangdong region alone has left ~302 abandoned mines, 191 million tons tailings and 153 km² of destroyed forests.

In June 2011, in an effort to regulate the industry and deal with the environmental effects, the Chinese government enforced a ban on surface mining and batch/heap leaching while implementing mandatory in-situ leaching technology for the processing of the ion-adsorption clays, as being more advantageous in terms of surface vegetation clearing and soil disturbance. The basic principle of in-situ leaching (also called “solution mining”) is injection of leaching solution directly into the natural orebody and retrieval of the pregnant solutions for further processing. Leaching holes with a depth of 1.5-3 m and diameter of ~0.8 m are drilled 2-3 m apart, for up to 100 m, the lixiviant (~0.3 M (NH₄)₂SO₄) is injected at high pressure, flows through the pores of the orebody and the loaded leach solution is pumped above-ground through the recovery wells; the whole process (including injection of water for washing) can take up to 400 days and ultimately 85-90% of REE are extracted.

The in-situ leaching technique is also currently applied in China for the recovery of residual REE from the tailings of older batch and heap leaching operations.

The implementation of in-situ leaching requires comprehensive geological surveys - specific to each site - in order to determine the hydrogeological structure of the area, ore characteristics, grade, orientation and the surrounding rock infiltration properties. The procedure can only be applied to an orebody with suitable permeability and placed over solid bedrock without fissures. Failure to conduct diligent geological surveys may result in serious environmental degradation such as underground water contamination, mine collapse, landslides and severe loss of REE recovery.

V. Evaluation of Leaching Potential of Various Ion-adsorption Clays at University of Toronto

As new ion-adsorption REE deposits are being explored and discovered in the rest of the world, research on REE extraction from clays has expanded outside of China as well. For the last five years, the University of Toronto has conducted systematic
in-depth studies on the leaching chemistry and optimum conditions for REE extraction from clay samples obtained from various geographical locations. Overall, it was determined that, under atmospheric conditions, the leaching power of monovalent ions for REE extraction depends on the hydration energy of the exchange ion, following the order Cs+ > NH4+ > Na+ > Li+, in both sulphate and chloride. Batch leaching studies also revealed that the ion exchange process achieved equilibrium in as little as 5 minutes, regardless of the experimental conditions; ambient temperatures and moderately acidic pH values (4-5) represent optimum conditions for maximum REE recovery.

Based on those previous studies, a benchmark leaching procedure was established and research has been conducted at the University of Toronto in order to compare leaching characteristics among different clay samples obtained from Africa, Asia and South America and evaluate lanthanide extraction. The final aim is to develop a fully contained optimized process for field implementation that minimizes the impact to environment by providing options for efficient reagent use, maximized extraction and recycle/regeneration of the lixiviant.

**Experimental**

**Solid Characterization**

The REE contents of the clay samples were determined by acid digestion at 220°C, using the Ethos EZ microwave digestion system, followed by inductively coupled plasma optical emission spectrometry of the solution (Agilent 720 ICP-OES).

**Batch Leaching Tests**

The leach solutions were prepared using ACS reagent grade ammonium sulphate and deionized water. The benchmarked procedure for leaching is: 0.5M (NH4)2SO4 (natural pH ~ 5.2), ambient conditions, liquid to solid (L:S) ratio of 2:1 (vol./mass), 30 minutes total time. The slurry was agitated via magnetic stirring then the mother liquor was separated by vacuum filtration. The filter cake was washed by deionized water, and the wash water was collected separately for analysis. The resultant solutions were diluted with 5% (vol.) nitric acid and analysed by ICP-OES to calculate the REE extractions.

**Results and Discussion**
Table 1 shows the REE content (as %wt.) of the various clay samples tested while Table 2 shows the relative distribution of individual REE in the clays.

**Table 1**: REE content of ion-adsorption clays from different geographical origins

<table>
<thead>
<tr>
<th>Origin</th>
<th>Africa</th>
<th>Asia</th>
<th>South America</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A1</td>
<td>A2</td>
<td>A3</td>
</tr>
<tr>
<td>REE (wt%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>0.029</td>
<td>0.014</td>
<td>0.018</td>
</tr>
<tr>
<td>La</td>
<td>0.175</td>
<td>0.029</td>
<td>0.179</td>
</tr>
<tr>
<td>Ce</td>
<td>0.026</td>
<td>0.017</td>
<td>0.022</td>
</tr>
<tr>
<td>Pr</td>
<td>0.028</td>
<td>0.007</td>
<td>0.027</td>
</tr>
<tr>
<td>Nd</td>
<td>0.100</td>
<td>0.023</td>
<td>0.088</td>
</tr>
<tr>
<td>Sm</td>
<td>0.017</td>
<td>0.004</td>
<td>0.017</td>
</tr>
<tr>
<td>Eu</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Gd</td>
<td>0.011</td>
<td>0.004</td>
<td>0.009</td>
</tr>
<tr>
<td>Tb</td>
<td>0.002</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Dy</td>
<td>0.006</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Ho</td>
<td>0.001</td>
<td>0.001</td>
<td>4.60E-04</td>
</tr>
<tr>
<td>Er</td>
<td>0.002</td>
<td>0.001</td>
<td>0.015</td>
</tr>
<tr>
<td>Tm</td>
<td>2.00E-04</td>
<td>8.69E-05</td>
<td>6.85E-05</td>
</tr>
<tr>
<td>Yb</td>
<td>0.002</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Lu</td>
<td>2.66E-04</td>
<td>2.66E-04</td>
<td>2.53E-04</td>
</tr>
<tr>
<td>TREE</td>
<td>0.399</td>
<td>0.108</td>
<td>0.380</td>
</tr>
</tbody>
</table>

Despite total rare earth element (TREE) content being consistent with grades expected for the ion-adsorption clays, no specific pattern of preferential REE accumulation and distribution was observed, except that all ores seem to be rich in La and Y and Nd; although some similarities in terms of relative composition are observed within clays originating from the same geographical areas (e.g. A1 through A5), there is no consistent trend. This is probably due to wide variations in composition of original host rocks and incongruent dissolution-adsorption processes during the weathering processes.
Table 2: Relative distribution of REE within clay samples

<table>
<thead>
<tr>
<th>Origin</th>
<th>Africa</th>
<th>Asia</th>
<th>South America</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A1</td>
<td>A2</td>
<td>A3</td>
</tr>
<tr>
<td>REE (%REE)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>7.2</td>
<td>12.9</td>
<td>4.6</td>
</tr>
<tr>
<td>La</td>
<td>43.8</td>
<td>26.8</td>
<td>47.0</td>
</tr>
<tr>
<td>Ce</td>
<td>6.4</td>
<td>16.1</td>
<td>5.7</td>
</tr>
<tr>
<td>Pr</td>
<td>7.0</td>
<td>6.1</td>
<td>7.2</td>
</tr>
<tr>
<td>Nd</td>
<td>24.9</td>
<td>21.6</td>
<td>23.2</td>
</tr>
<tr>
<td>Sm</td>
<td>4.4</td>
<td>4.1</td>
<td>4.4</td>
</tr>
<tr>
<td>Eu</td>
<td>0.2</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Gd</td>
<td>2.8</td>
<td>3.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Tb</td>
<td>0.4</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Dy</td>
<td>1.4</td>
<td>2.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Ho</td>
<td>0.2</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Er</td>
<td>0.6</td>
<td>1.2</td>
<td>4.0</td>
</tr>
<tr>
<td>Tm</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Yb</td>
<td>0.4</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Lu</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>TREE</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

The clay samples listed in Table 1 were leached using the benchmarked procedure described above to investigate the terminal REE extraction levels (shown in Table 3) and TREE leaching kinetics, respectively (presented in Figure 4).

From data in Table 3 it can be observed that all the minerals investigated are the ion-adsorption type, i.e., the lanthanides are physically adsorbed and can be easily recovered via a simple ion-exchange leaching procedure, as described by Moldoveanu and Papangelakis.9,10 The extraction levels vary between 40 to 80%, consistent with the predicted exchangeable REE percentage, as described by Chi and Tian8. Again, there is no consistent trend regarding REE desorption within clays of similar geographical origin; this could be explained in terms of:

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(1) The ores contain various mixtures of clay materials with different cation-adsorption capacities, i.e., clays with lower cation exchange capacity (CEC) such as kaolinite will adsorb less ions than the ones with larger CEC such as smectites, hence less is available for desorption (possible observed for clays A4 and A5).

(2) The overall exchangeable fraction of REE is low, regardless of the high REE content, the balance being the matrix-bound lanthanides (possible observed for clays C1).

As a general common trend for all clays, cerium does not exhibit large extraction due to its presence mostly as CeO₂ while some of the heavy REE also show poor extraction probably because of the stronger adsorption, as described by Coppin et al.²⁰

Table 3. Final REE extraction from ion-adsorption clays from different geographical origins

<table>
<thead>
<tr>
<th>Origin</th>
<th>Africa</th>
<th>Asia</th>
<th>South America</th>
</tr>
</thead>
<tbody>
<tr>
<td>%E</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>77.3</td>
<td>80.5</td>
<td>70.8</td>
</tr>
<tr>
<td>La</td>
<td>83.6</td>
<td>85.0</td>
<td>82.9</td>
</tr>
<tr>
<td>Ce</td>
<td>0.0</td>
<td>0.0</td>
<td>35.6</td>
</tr>
<tr>
<td>Pr</td>
<td>75.1</td>
<td>62.9</td>
<td>72.8</td>
</tr>
<tr>
<td>Nd</td>
<td>80.8</td>
<td>86.3</td>
<td>83.2</td>
</tr>
<tr>
<td>Sm</td>
<td>90.6</td>
<td>43.1</td>
<td>76.9</td>
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<tr>
<td>Eu</td>
<td>62.1</td>
<td>61.3</td>
<td>36.2</td>
</tr>
<tr>
<td>Gd</td>
<td>82.6</td>
<td>90.1</td>
<td>61.6</td>
</tr>
<tr>
<td>Tb</td>
<td>84.1</td>
<td>91.5</td>
<td>35.6</td>
</tr>
<tr>
<td>Dy</td>
<td>80.9</td>
<td>87.5</td>
<td>61.5</td>
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<tr>
<td>Ho</td>
<td>75.5</td>
<td>82.9</td>
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<tr>
<td>Er</td>
<td>86.8</td>
<td>75.2</td>
<td>53.0</td>
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<td>53.4</td>
<td>57.9</td>
<td>47.0</td>
</tr>
<tr>
<td>Yb</td>
<td>73.2</td>
<td>77.9</td>
<td>61.9</td>
</tr>
<tr>
<td>Lu</td>
<td>52.3</td>
<td>78.5</td>
<td>51.5</td>
</tr>
<tr>
<td>TREE</td>
<td>76.6</td>
<td>80.3</td>
<td>68.7</td>
</tr>
</tbody>
</table>

In terms of extraction kinetics, all materials investigated showed a common trend of fast REE desorption which is the typical behaviour of the ion-adsorption minerals. While each clay sample possesses a slightly different REE content and REE extraction end point, it can be seen that extractions reach the terminal levels in a very similar fashion, typically reaching plateau in less than 15 minutes of batch
The authors demonstrated that desorption kinetics are very fast independently of leaching conditions such as temperature, pH, and agitation, which influence only terminal extraction levels.

**Figure 4:** Kinetic response of ion-adsorption clays from various geographical origins to benchmark leaching conditions (0.5M (NH₄)₂SO₄, 60 min leaching under ambient conditions)

**Conclusions**

Past and ongoing research conducted at University of Toronto demonstrated the existence and commercial potential of ion-adsorption clay deposits outside China and established a unified benchmark procedure for REE leaching from these types of minerals. It was found that, in spite of variations in clay origin and REE content,
all REE consistently reached peak extraction levels under ambient conditions with fast kinetics. However, the terminal extractions were generally clay and element-specific.
Based on those studies, an optimized process ready for field implementation is currently being developed, that highly minimizes the impact to environment by providing options for efficient reagent use, maximized extraction and recycle/regeneration of the lixiviant.

Acknowledgements

The authors would like to thank Molycorp Inc. and Tantalus Rare Earth A.G for providing clay samples.

References

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ADVANCING KEY TECHNOLOGIES FOR REE MINERAL PROCESSING

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Abstract
UIT Dresden has scrutinised several recent investigations on optimisation potential for alternative extraction and processing of technologically critical, high-demand REEs from some primary and secondary REE deposits: (1) Ion-adsorption clays as current global main source of heavy REE (e.g. Dysprosium, Terbium), (2) Monazite ore as main source of light-middle REE (e.g. Neodymium) but also NORM (e.g. Thorium, Uranium, Radium), and (3) Mine tailings as alternative source of REE (mainly Cerium). Extraction and processing of REE from ion-adsorption clays stands out as being easily accessible with relatively low capitalisation and operational costs, low NORM content. Extraction from ion-adsorption clays may have high remediation costs depending on extraction method. Monazite processing is considered high-risk due to locally high Thorium content with challenges for sustainable disposal. REE extraction from tailings through heap-leaching shows potential for low-cost recovery, but many tailings do not contain the high-value heavy REE required to make such REE recovery economical.

Introduction
Recent commodity studies indicate heavy Rare Earth Elements (REE) as most critical mineral resource throughout the next decades as these resources are among the main sources for innovative ‘green’ technologies for energy generation and e-mobility. However, current R&D projects place little effort on research and development of the key issues related to (heavy) REE mining and extraction which include (1) Development of more economic, alternative and environmentally, socially and economically sustainable metallurgical REE extraction technologies, and (2) Removal (and re-utilization) of naturally occurring radioactive material (NORM) from the REE mineral processing stream. The exploration and mineral processing industry is facing these challenges regardless of previous, current or future market prices of technology metals, unless substitute materials enter the market on an industry scale.

In response to the expected shortage of technology metals in high-tech industry countries, numerous (non-China) REE deposits are currently being developed throughout the world (status May 2014: 57 reporting code-compliant REE projects;
TechMetalResearch, May 2014), buts many projects seem to be lingering at, or do not pass the scoping or prefeasibility stage as their capital and operating costs are high.

Western world REE projects generally possess higher capitalisation costs for metallurgical plant setup and operational costs for hydrometallurgical REE extraction, concentration, and separation of rare earth oxides. Numerous feasibility studies have shown that large scale commercial operations are required; such large scale rare earth production is currently lacking in Europe. The quest for economic (lower cost) extraction, processing and separation of REE is, and will remain, among the most important challenges for any REE project regardless of REE market price fluctuations.

A second challenge is economic recovery. Many REE deposits throughout the world show appreciable REE content, but very few deposits contain the desired high value and technologically critical heavy REEs content (e.g. Dysprosium, Terbium, Europium), which are required to make REE mining and processing economical. Without the high-value REE content, metallurgical REE processing facilities are required to process unrealistically large amounts of low-moderate value REE ore for economic REE recovery. In addition, the metallurgical processes required to isolate individual REE metal species are complex and every REE deposit requires a different processing chain, or at least some modification and optimisation within the metallurgical processing chain for optimal recovery.

A third challenge is NORM removal from REE ore. All minerals with economically relevant REE content (bastnaesite, monazite, steenstrupine, xenotime, ± eudialyte, ± allanite) contain naturally occurring radioactive material (NORM); some monazite ore contains up to 12 wt.% of Thorium (e.g. Steenkampsraal, South Africa). Processing of ore with economic REE quantities tends to accumulate substantial NORM content and standard metallurgical laboratories in Europe are generally not equipped or licenced for large-stream NORM material separation. Outside of Europe, high-volume REE processing facilities for NORM include the Lynas Advanced Materials Plant (LAMP) in Gebeng industrial estate in Kuantan, Malaysia, for processing of monazite ore from Mt. Veld from Western Australia, and in India there is a state run operation which treats Monazite concentrates which are high in NORMs.

A fourth challenge, but also an opportunity, is REE extraction from mining tailings. Mining tailings are pre-processed, typically silt-size materials which can be enriched in REE depending on the former main resource; for instance former uranium mining tailings tend to show REE enrichments. This study discusses a project in Queensland, Australia, where former uranium mine tailings show some economic light REE-enrichment where one main challenge lies in optimized heap-leaching design with sufficient light REE recovery.
UIT Dresden has developed several conceptual approaches for potential low- 
moderate cost potential projects with optimised extraction schemes from primary and 
secondary REE deposits: (1) **ion-adsorption clays** as current main source of heavy REE 
(e.g. Dysprosium, Terbium), (2) **Monazite** ore as main light-middle REE (e.g. 
Neodymium) yet also NORM (e.g. Thorium, Uranium, Radium) bearing ore, and (3) **Mine tailings** as alternative source of light REE (e.g. Cerium). By discussing type 
examples for REE deposits, we present preliminary results from some prefeasibility 
and feasibility studies, and outline selected research opportunities in REE extraction 
and NORM separation technology. The results find direct application in our own 
affiliated mining operations and consulting projects worldwide. The ion-adsorption 
clay project is in direct response to official requests by Govt. for development of 
sustainable leaching technologies.

**REE Recovery from Ion-Adsorption Clays**

Ion-adsorption clays are currently the world’s main source of heavy REE which contain 
some of the most critical technology metals as shown by the United States Geological 
Survey (USGS), the British Geological Survey (BGS), and the European Commission. For 
instance, the main current supply of Dysprosium (Dy) are ion-adsorption clays in the 
Xunwu and Longnan province, southern China, followed by xenotime minerals at 
Dubbo Zirconia (Australia) and Kvanefjeld (Greenland). Based on current forecasts, the 
Dy supply cannot meet short- and/or long-term demand (until 2050); not even when 
including Dy from recycling products.

REE enriched ion-adsorption clays are known from the equatorial belt around the 
globe (tropical high-humidity climate with intense chemical weathering), notably Mt. 
Weld Australia, Araxa Brazil, Kangangunde Malawi and the Tantalus project 
Madagascar, but currently all economically important REE-rich ion-adsorption clays 
deposits are situated in southern China where ion-adsorption clay mining for more 
than two decades led to the China monopole in heavy REE production. REE-rich ion-
adsorption clays typically consist of saprolite and kaolinitic clays (Xunwu and Longnan) 
containing microcrystals of bastnaesite, synchisite and allanite adsorbing the \( \text{RE}^{3+} \) ions 
with typical concentrations of 0.05-0.2% REO, out of which 2% tend to consist of 
Dysprosium. If weathering occurred above REE-enriched alkaline granitoids they may 
show enrichments in heavy REE as the soluble light REE are being mobilised during 
weathering processes.

At Longnan, China, large parts of the heavy REE production from ion-adsorption clays 
are produced by in-situ leaching and surface/mountain-top mining by tank/heap 
leaching with ammonium sulfate and Na-chloride. REE in-situ leaching produces large 
environmental issues as the leaching solutions are difficult to control. With increased
environmental controls and operating standards the operating costs are expected to increase significantly.

The leaching chemistry in in-situ recovery (ISR) operations revolves around acid dissolution of matrix minerals and/or complexation of the REE into solution (especially in ion-adsorption clays). The latter can be achieved with various organic molecules that can be generated through bacteria in or ex situ. Common complexing reagents used in the context of REE processing are citric and lactic acid. Inorganic ligands have also been explored, such as NaCl or (NH₄)₂SO₄, with good results. Table 1 shows a comparison of REE concentrations in ion-adsorption clay profiles and bastnaesite, xenotime and monazite.

**Table 1**: Rare Earths content of major source minerals in China (in % total REO; sources: Roskill 2011, USGS 2011).

<table>
<thead>
<tr>
<th>Rare Earth Oxide</th>
<th>Bastnaesite Bayan Obo</th>
<th>Xenotime Guangdong</th>
<th>Ion-Adsorption Clays</th>
<th>Monazite Guangdong</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Light</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La₂O₃</td>
<td>23.0</td>
<td>1.2</td>
<td>42.0</td>
<td>1.8</td>
</tr>
<tr>
<td>CeO₂</td>
<td>50.0</td>
<td>3.0</td>
<td>2.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Pr₆O₁₁</td>
<td>6.2</td>
<td>0.6</td>
<td>8.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>18.5</td>
<td>3.5</td>
<td>30.8</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm₂O₃</td>
<td>0.8</td>
<td>2.2</td>
<td>3.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Eu₂O₃</td>
<td>0.2</td>
<td>0.2</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Gd₂O₃</td>
<td>0.7</td>
<td>5.0</td>
<td>2.9</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>Heavy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb₄O₇</td>
<td>0.1</td>
<td>1.2</td>
<td>Trace</td>
<td>1.3</td>
</tr>
<tr>
<td>Dy₂O₃</td>
<td>0.1</td>
<td>9.1</td>
<td>Trace</td>
<td>6.7</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>Trace</td>
<td>59.3</td>
<td>8.0</td>
<td>65.0</td>
</tr>
<tr>
<td>Total</td>
<td>99.6</td>
<td>85.3</td>
<td>99.1</td>
<td>88.7</td>
</tr>
</tbody>
</table>

Technical issues with ion-adsorption clay mining by in-situ leaching include the conditioning of the lateritic soil profile regarding permeability. At Longnan, REE concentration in sample location tends to be highest at shallow depths of 3-7m. Standard ISR operation require saturated host rock conditions plus a critical hydraulic head above the ISR pump (typically >45m hydraulic head), which rules out standard ISR mining technology for recovery of shallow REE mineralization from ion-adsorption clays but requires a modified approach. UIT Dresden is currently conducting a research initiative (supported by the German Ministry of Economics and Research...
BMBF) on extraction of ion-adsorption clays from Madagascar (Tantalus project). The goal of this project is to develop an optimized extraction technology for heavy REE recovery from ion-adsorption clays through in-situ/heap leaching technology. The focus of this R&D project includes:

1. the geotechnical improvement of permeability of ion-adsorption clays in laterite and saprolite,
2. the development of alternative bio-hydrometallurgical REE extraction technologies for selective and sustainable REE extraction,
3. process simulation of extraction and separation of adsorptive-bonded REE as base for optimisation of REE extraction by using thermodynamic and experimental data.

One goal of this project between UIT Dresden, the Helmholtz Centers of Resource Technology and Resource Ecology, GUB Engineering AG, IPK Gatersleben and GMBU Society for Support of Medical-, Bio- and Environmental Technologies, is a re-assessment of and optimisation of existing hydrometallurgical extraction and separation methods with development of new biotechnological extraction methods regarding minimised processing costs and environmental footprint.

**REE Recovery from Monazite Ore**

Monazite, a REE-bearing phosphate, is a typical ingredient of placer deposits and known for its light-medium REE content (mainly Lanthanum, Cerium and Neodymium), but can also contain heavy REEs (particularly Yttrium; *Ni et al., 1995*). Monazite is a major source of Neodymium which ranks among the high-demand and critical technology elements for magnets used in wind generators; Neodymium is among the key ingredients for wind-power generators as state-subsidised form of 'green' alternative energy in Germany and other states in Europe.

However, monazite is also an important carrier of NORM. Typical monazite generally contains 4.5–9.5% Thorium as ThO₂, and 0.2–0.4% Uranium as U₃O₈, depending on the region of mineral origin (*Table 2*). When decay products of either are present in the minerals, the radioactivity levels may be significant as monazite is concentrated in the processing stream. Typical Indian plant processings are in the order of 3,000-4,000 tons/year of monazite.
**Table 2:** Typical radionuclide content of some REE mineral ores in % of composition (Source: IAEA NORM V Proceedings 2008).

<table>
<thead>
<tr>
<th></th>
<th>Total Rare Earth Oxides</th>
<th>$\text{U}_3\text{O}_8$</th>
<th>$\text{ThO}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monazite, Australia</td>
<td>61.33</td>
<td>0.34</td>
<td>6.55</td>
</tr>
<tr>
<td>Monazite, India</td>
<td>59.68</td>
<td>0.37</td>
<td>9.58</td>
</tr>
<tr>
<td>Monazite, Malaysia</td>
<td>59.65</td>
<td>0.24</td>
<td>5.90</td>
</tr>
<tr>
<td>Monazite, Thailand</td>
<td>60.20</td>
<td>0.44</td>
<td>5.76</td>
</tr>
<tr>
<td>Monazite, Rep. of Korea</td>
<td>60.20</td>
<td>0.45</td>
<td>5.76</td>
</tr>
<tr>
<td>Monazite, DPRK</td>
<td>42.65</td>
<td>0.18</td>
<td>4.57</td>
</tr>
</tbody>
</table>

**Table 3** shows a comparison of radioactivity resulting from processing of different ore minerals, with specific reference to monazite concentrate.

**Table 3:** Radioactivity in mineral sands (Source: IAEA 2003 Tech Report 419).

<table>
<thead>
<tr>
<th></th>
<th>Thorium ppm</th>
<th>Thorium Bq/g</th>
<th>Uranium ppm</th>
<th>Uranium Bq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore</td>
<td>5 - 70</td>
<td>0.04 – 0.60</td>
<td>3 - 10</td>
<td>0.07 – 0.25</td>
</tr>
<tr>
<td>Heavy mineral concentrate</td>
<td>80 - 800</td>
<td>0.60 – 6.6</td>
<td>&lt;10 - 70</td>
<td>&lt;0.25 – 1.70</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>50 - 500</td>
<td>0.40 – 4.1</td>
<td>&lt;10 - 30</td>
<td>&lt;0.25 – 0.75</td>
</tr>
<tr>
<td>Rutile</td>
<td>&lt;50 - 350</td>
<td>&lt;0.40 – 2.9</td>
<td>&lt;10 - 20</td>
<td>&lt;0.25 – 0.50</td>
</tr>
<tr>
<td>Zircon</td>
<td>150 - 300</td>
<td>1.2 – 2.5</td>
<td>150 - 300</td>
<td>3.7 – 7.4</td>
</tr>
<tr>
<td><strong>Monazite</strong> concentrate</td>
<td>10,000 – 55,000</td>
<td>80 – 450</td>
<td>500 – 2,500</td>
<td>12 – 60</td>
</tr>
<tr>
<td>Processing tailings (incl. monazite)</td>
<td>200 – 6,000</td>
<td>1.5 – 50</td>
<td>10 – 1,000</td>
<td>0.25 – 25</td>
</tr>
<tr>
<td>Bastnaesite</td>
<td>58 - 74</td>
<td>---</td>
<td>0.11 – 0.20</td>
<td>0.64 – 0.94</td>
</tr>
<tr>
<td>Xenotime, Malaysia</td>
<td>54.00</td>
<td>0.81</td>
<td>0.83</td>
<td>26.20</td>
</tr>
<tr>
<td>Gadolinite</td>
<td>32 - 46</td>
<td>---</td>
<td>&lt;2</td>
<td>---</td>
</tr>
</tbody>
</table>

When processing monazite, the Thorium hydroxide cake produced during the extraction of REEs from monazite contains the U fraction as well as the unreacted monazite. The quantity generated amounts to 250kg per 1ton of monazite processed.

Solvent extraction with tributyl phosphate (TBP) from an aqueous 8 N nitric acid solution of Thorium and mixed REE permits the recovery of Thorium, Uranium, Cerium, and Cerium-free REE from monazite. Other commercially significant processes involve precipitation of Thorium pyrophosphate or basic salts from the leach liquor and
subsequent recovery of the REE in solution as double sulfates, fluorides, or hydroxides or even selective solubilisation of Thorium in the ore treatment stage itself.

The sulfuric acid process (acid baking) is used at the Lynas Advanced Materials Plant in Malaysia. Here concentrated sulphuric acid is contacted with monazite concentrated at 650 deg C. In another industrial process (caustic cracking), fine ground monazite is generally attacked with a 60-70% sodium hydroxide solution at 140-150°C. Previously, grinding and caustic digestion were performed as one step which enabled ~50% savings in caustic soda consumption. This yielded a clean separation by digesting the ore with caustic soda at 170°C under a pressure of several atmospheres. The mixed RE-Thorium hydroxide cake is processed for REE and Thorium recovery by a variety of methods.

The radioactive equilibrium of the Th-232 chain is broken at the acid extraction stage. Thereafter the buildup and decay of activity at different stages follow separate routes. The activity inventory at various stages is marked by disequilibria and the activity at each stage has to be accounted for by taking the material balance, fractionation and buildup/decay. Hazards from Thorium may result from both external and internal sources. External hazards are due to high energy beta and gamma rays, while internal hazards are mainly due to alpha emitting radionuclides deposited inside the body.

In Europe, mineral processing facilities are required to account for accumulation of Thorium during extraction and processing, but NORM processing facilities are lacking. However, UIT Dresden is currently in the process of expanding its laboratory facilities to include hydrometallurgical processing of NORM material from mineral concentrate consistent with IAEA regulations. IAEA provides regularly updated exemption levels. A material is exempted without further consideration if the effective dose expected to be incurred by a member of the public is of the order of 10 μSv/yr, or less. Where bulk quantities of radionuclides are involved, IAEA makes provision for exemption using a dose criterion commensurate with natural background levels, that is about 1 mSv/yr. This criterion is satisfied if the activity concentration does not exceed 1 Bq/g for uranium and thorium series radionuclides, and 10 Bq/g for $^{40}$K (IAEA Safety Guide Level No. RS-G-1.7, 2004; Chambers et al., 2010).

The activity concentration criteria of 1 Bq/g for Uranium and Thorium series radionuclides and 10 Bq/g for $^{40}$K are generally accepted as the most practicable way forward in determining which materials should be considered for regulation in terms of the requirements for practices. A dose criterion of the order of 1 mSv per year is now commonplace as a de facto standard for exemption of NORM from the regulatory requirements for practices. For a plant processing of 3,000-4,000 t/year of monazite,
the individual annual exposures for the past 25 years were in the range of 3-9 mSv. The representative exposure for REE production are 0.64 man mSv (standard deviation 0.19 man mSv) per ton of REE concentrate produced by chemical processing of monazite.

**REE Recovery from Mining Tailings**

UIT Dresden has developed initial heap leaching concepts for REE recovery and seeks to pursue a feasibility study for leaching REE from former Uranium mining tailings. Mary Kathleen is a former Uranium mine (excavated between the 1950’s and 1980’s) with relatively high REE content, and the only commercial example of a REE-U skarn deposit. While Uranium (present as uraninite in fine disseminations enclosed in allanite at about 35% of the ore at outcrop, usually replacing garnet) was mined and processed, the REE were not recovered and consequently significant REE concentrations are present (documented) in the unprocessed waste rocks and tailings (milling residues). The West Tip waste rock samples at Mary Kathleen (La up to 7,310 ppm, Ce up to 11,600 ppm, U up to 916 ppm) show two times the concentration of Ce, La and U compared to Stockpile and Crusher pile samples; this could be a priority site for initial reprocessing. The sampled mineralogy comprises mainly garnet, clinopyroxene, allanite, chlorite, calcite, pyrite, and locally apatite. An overview of REE content in Mary Kathleen mining tailings is shown in Table 4.

Up until now there were no plans to recover the 4.4% total Rare Earths oxides (TREO) in the existing tailings dam. About 9.2 million tons of ore were milled with ore grades of 0.10-0.15% U₃O₈ (source: ASX Announcement Universal Resources 2007) so that it is assumed that there are approximately 7 million tons of ore tailings at the site in a purpose-built dam structure with about 3% TREO mainly in allanite and stillwellite as economically relevant REE minerals, making it one of the largest light REE deposits (mainly La, Ce) in Australia. Although tailings reprocessing could be economically attractive for mining projects in Europe, the lack of NORM processing facilities prevents this project from being economically feasible.
Table 4: Calculation of REE content (in %REO and value) in Mary Kathleen tailings with price comparison (as of April 22, 2013) relative to other major REE deposits. From a value basis, the Mary Kathleen tailings appear to be at the least-value end of the REO market due to their paucity of HREE where the current value (and scarcity) lies. A Mary Kathleen tailings play would be a mostly Cerium/Lanthanum commodity play which would only be interesting if there would be a very inexpensive method of extracting REO from the tailings so that one would not have to compete purely on price.

<table>
<thead>
<tr>
<th></th>
<th>22-Apr-13</th>
<th>Mary Kathleen</th>
<th>Mt Weld</th>
<th>Mountain Pass</th>
<th>Nolans Bore</th>
<th>Kvanefjeld</th>
<th>Balyunebo</th>
<th>Thor Lake Basal Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Price (USD)</td>
<td>% Value</td>
<td>% Value</td>
<td>% Value</td>
<td>% Value</td>
<td>% Value</td>
<td>% Value</td>
<td>% Value</td>
</tr>
<tr>
<td>La oxide</td>
<td>La2O3</td>
<td>9.6</td>
<td>33.5</td>
<td>3.22</td>
<td>25.5%</td>
<td>2.45</td>
<td>33.0%</td>
<td>3.17</td>
</tr>
<tr>
<td>Ce oxide</td>
<td>CeO2</td>
<td>9.6</td>
<td>51.5</td>
<td>4.94</td>
<td>46.7%</td>
<td>4.48</td>
<td>49.0%</td>
<td>4.70</td>
</tr>
<tr>
<td>Nd oxide</td>
<td>Nd2O3</td>
<td>72</td>
<td>9.1</td>
<td>6.55</td>
<td>18.5%</td>
<td>13.32</td>
<td>13.0%</td>
<td>9.36</td>
</tr>
<tr>
<td>Pr oxide</td>
<td>Pr2O3</td>
<td>80</td>
<td>4</td>
<td>3.20</td>
<td>5.3%</td>
<td>4.26</td>
<td>4.0%</td>
<td>3.20</td>
</tr>
<tr>
<td>Sm oxide</td>
<td>Sm2O3</td>
<td>25</td>
<td>0.006</td>
<td>0.00</td>
<td>2.3%</td>
<td>0.57</td>
<td>5.0%</td>
<td>1.25</td>
</tr>
<tr>
<td>Dy oxide</td>
<td>Dy2O3</td>
<td>630</td>
<td>0.05</td>
<td>0.32</td>
<td>1.1%</td>
<td>0.78</td>
<td>0.00</td>
<td>0.4%</td>
</tr>
<tr>
<td>Eu oxide</td>
<td>Eu2O3</td>
<td>425</td>
<td>0.05</td>
<td>0.63</td>
<td>0.1%</td>
<td>0.78</td>
<td>0.00</td>
<td>0.2%</td>
</tr>
<tr>
<td>Tb oxide</td>
<td>Tb4O7</td>
<td>1100</td>
<td>0.02</td>
<td>0.22</td>
<td>0.0%</td>
<td>0.08</td>
<td>0.1%</td>
<td>0.88</td>
</tr>
<tr>
<td>Y oxide</td>
<td>Y2O3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.4%</td>
<td>0.00</td>
<td>7.7%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>19.07</strong></td>
<td><strong>31.47</strong></td>
<td><strong>22.93</strong></td>
<td><strong>34.42</strong></td>
<td><strong>30.10</strong></td>
<td><strong>27.15</strong></td>
<td><strong>116.95</strong></td>
</tr>
</tbody>
</table>
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Unlocking Rare Earth Elements from European apatite-iron ores

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Abstract

Rare Earth Elements are known to occur within apatite-magnetite ores of the Kiruna type. Previously it was assumed that the REE was associated to the apatite part of the ore. It is now shown that the REE follows the apatite to a much less degree, and that the REE are contained in the minerals monazite, allanite and some unknown REE-phase still to be identified. Monazite occurs as inclusions in the apatite as well as free particles. Allanite is to some degree in mixed grains with magnetite but also in free particles. Monazite mainly reports to the apatite concentrate while allanite largely goes to the tailings. Laboratory flotation also shows some preferential concentration of heavy REE over light REE to the apatite concentrate. A new EU project, REEcover, will characterise the REE phases in this type of iron ore and among the different process streams within the mineral beneficiation chain.

Introduction

Deposits of apatite iron ores are the major source for iron in the European Union and are exploited by LKAB in several mines in the Kiruna area in northern Sweden, which is an important mining province dominated by Fe and Cu deposits. The combined production from two large underground mines and one open pit was for 2013 25.5 M tonnes of pellets and fines and a total ore production of 2275 M tonnes from 11 mines during the last 127 years. These magnetite deposits with/without haematite have mineralogical and textural features that are different to most other types of iron deposits in the world. Most characteristic is the presence of apatite as an important gangue mineral, which contributes to high phosphorus content of the ores. Many apatite iron ores contain 1 to 5 % P on average and apatite has been produced as a by-product at Malmberget during the First and Second World War but also in 1952-1953. In the Kiruna area, apatite has been produced from the Rektorn deposit in 1942 to 1946, and 1985-1988 about 0.4 Mt apatite concentrates were produced by flotation
from Kiirunavaara ore\textsuperscript{1}. Elevated contents of rare earth elements (REE) in apatite from the apatite iron ores in Northern Sweden was early noticed and investigated in some detail in the 1960’s\textsuperscript{2}. The samples then consisted of gangue minerals from different ores, flotation concentrates of apatite and handpicked apatite grains. These results demonstrated a strong enrichment of the LREE in apatite with total REE+Y contents of 1545 to 8855 ppm and that Monazite occurred as inclusions in Apatite\textsuperscript{2}. In a recent study\textsuperscript{3}, the chemistry and occurrence of REE-minerals in the Kiirunavaara deposit have been further investigated by optical microscopy, scanning electron microscope (SEM) and electron micro probe analysis (EMPA). The samples included apatite concentrates obtained from tailings and ore from drill cores. This study confirmed previous results but showed that allanite and monazite may be common as larger grains in the ore and act as important carrier of the light rare earth elements.

TEXTURE AND CHEMISTRY OF REE-BEARING MINERALS

Three main REE-bearing minerals have been identified by optical microscopy, SEM and EMP analysis and analysed for their chemical composition by electron micro probe\textsuperscript{3}. Rarely grains of thorite with moderate enrichment of heavy rare earth elements were found.

Apatite

Apatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$ occurs mainly as disseminated grains in the ore or form band, schliren or veinlets. Disseminated apatite occurs interstitial to magnetite as subhedral and equidimensional or prismatic grains up to 0.5 mm large but mostly in the size of 0.05-0.1 mm. In banded type of D-ore, apatite often form prismatic grains with the long axis oriented parallel with the banding. Apatite forming patches-strings-schliren may by slightly coarser in grain size (up to 1mm) and occur together with varying amounts of biotite, magnetite and calcite. Locally there occur skeletal ore, which is coarse grained with apatite and/or carbonate occurring interstitial to tabular magnetite crystals.

The apatite is a fluorapatite with 3.75 % F and 0.06 % Cl on average. There is no significant variation in composition for apatite in the tailings and samples of ore. Total content of REE is not possible to obtain by EMPA, due to values below detection limits for most rare earth elements. Highest values were obtained for Ce, while La, Nd and Y were only detected in some apatite grains. Total contents for rare earth element oxides (REO) including only La, Ce and Nd are in the range of 0.04 to 0.91 with an average of 0.25 percent by weight (Table 1). Slightly higher REO contents in apatite has been reported in earlier studies\textsuperscript{4,5} (0.07 to 1.57 and averages of 0.38 to 0.85 percent by weight) from spot analyses on individual grains of apatite by EMPA and LA-ICP-MS
while complete REO-analyses of concentrates of apatite generated values from 0.45 to 1.04 percent by weight. All the reported data demonstrates a strong dominance for the light rare earth elements.

**Monazite**

Monazite \((\text{Ce,La,Nd,Th})\text{PO}_4\) occurs texturally in two different forms within the apatite crystals. The monazite inclusions are mainly forming rods oriented parallel to the c-axis of the apatite grains but may also be tabular with a more random orientation (Figure 1a). In most cases, inclusions are most abundant in the inner part of apatite grains while the rim often lacks inclusions (Figure 1b). The rod-shaped inclusions have a length of up to 80 \(\mu\)m but are most commonly 10-30 \(\mu\)m in size. The tabular shaped monazite inclusions are mostly 5-20 \(\mu\)m in size. The highest amount of monazite inclusions is found in larger apatite grains within veins and schliren, while disseminated more fine grained apatite in D-ore might lack visible inclusions. Inclusions of monazite are also rare in samples containing higher contents of biotite. Besides occurring as inclusions in apatite, monazite is also locally found as up to 150 \(\mu\)m large single grains together with magnetite and gangue minerals.

Total content of REO in monazite (La, Ce, Pr, Nd) varies between 68.87 and 71.87 with an average of 70.0 percent by weight (Table 1). Earlier reported chemical data \(^4\) for monazite from Kiirunavaara is similar in contents with REO (La-Dy) varying from 68.11 to 68.92 percent by weight.

**Allanite**

In general, allanite \(\text{Ca}(\text{REE,Ca})\text{Al}_2(\text{Fe}^{\text{II}},\text{Fe}^{\text{III}})(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O(OH)}\) is rare in samples containing apatite with abundant inclusions of monazite but is rather common in samples containing biotite. Allanite occurs partly as single grains in association with apatite but also strongly intergrown with magnetite in up to 1 mm large aggregates (Figure 1c). Euhedral grains of allanite may be up to 300 \(\mu\)m in size but most commonly allanite occur in fine grained and anhedral to subhedral aggregates together with apatite, biotite and locally chlorite (Figure 1d). The REO content (La, Ce, Pr, Nd) of allanite varies from approx. 15 to 25 with an average of 22.5 percent by weight and with dominance for the LREE (Table 1). Others reported \(^4\) values of approx. 25.5 % REO (La, Ce, Pr, Nd, Sm, Gd, Dy) for allanite from Kiirunavaara.
Figure 1. Micrographs of apatite, monazite and allanite from the Kiirunavaara deposit\(^3\)

a) photomicrograph of apatite grain with rod shaped and tabular inclusions of monazite, crossed nicoles b) photomicrograph of apatite (grey) with monazite inclusions mainly in the inner part of grains, crossed nicoles c) SEM backscatter micrograph of allanite (medium gray) intergrown with magnetite (light gray) and apatite (dark grey) d) photomicrograph of apatite (ap) with some biotite (bi), chlorite (ch), and aggregates of allanite (al).

MATERIALS AND METHODS

This part is an update on earlier reported flotation results\(^7\). The materials received at LTU were: General sample consisting of sub-samples from a large number of drill-holes in the tailings pond, 5.85 % P\(_2\)O\(_5\) and \(\approx1250\) mg/kg REE; Coarse, low-phosphorus sample, 3.8 % P\(_2\)O\(_5\); Fine high-phosphorus sample, 6.6 % P\(_2\)O\(_5\). Both the general sample and the coarse product have wide particle size distributions, cf. Figure 2. A visual inspection of the samples gave that this was due to pebble chips, size 5-10 mm, from the pebble mills. These chips must be removed prior to any flotation. They may be removed by screening/wet classification or by grinding. A slight grinding is preferable since it will also fresh the mineral surfaces for flotation.
Table 1. Monazite, allanite and apatite from Kiruna tailings (% by weight)

<table>
<thead>
<tr>
<th>Mass- %</th>
<th>Monazite, n=11</th>
<th>S.D.</th>
<th>Allanite, n=14</th>
<th>S.D.</th>
<th>Apatite, n=39</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.18</td>
<td>0.11</td>
<td>32.66</td>
<td>1.51</td>
<td>0.07</td>
<td>0.09</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01</td>
<td>0.01</td>
<td>0.13</td>
<td>0.09</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.03</td>
<td>0.06</td>
<td>15.58</td>
<td>2.00</td>
<td>0.16</td>
<td>0.60</td>
</tr>
<tr>
<td>FeO</td>
<td>0.21</td>
<td>0.15</td>
<td>15.09</td>
<td>1.20</td>
<td>0.12</td>
<td>0.07</td>
</tr>
<tr>
<td>MnO</td>
<td>0.03</td>
<td>0.03</td>
<td>0.34</td>
<td>0.16</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00</td>
<td>0.01</td>
<td>0.32</td>
<td>0.10</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>0.13</td>
<td>0.07</td>
<td>11.97</td>
<td>1.76</td>
<td>54.55</td>
<td>0.53</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>BaO</td>
<td>0.03</td>
<td>0.04</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>14.816</td>
<td>1.879</td>
<td>6.989</td>
<td>3.06</td>
<td>0.020</td>
<td>0.042</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>37.840</td>
<td>0.857</td>
<td>11.442</td>
<td>1.826</td>
<td>0.200</td>
<td>0.160</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>11.951</td>
<td>1.106</td>
<td>2.446</td>
<td>1.106</td>
<td>0.027</td>
<td>0.050</td>
</tr>
<tr>
<td>Pr₂O₃</td>
<td>5.147</td>
<td>0.316</td>
<td>1.271</td>
<td>0.391</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>0.280</td>
<td>0.088</td>
<td>0.319</td>
<td>0.250</td>
<td>0.014</td>
<td>0.017</td>
</tr>
<tr>
<td>ThO₂</td>
<td>0.471</td>
<td>0.282</td>
<td>0.062</td>
<td>0.056</td>
<td>0.017</td>
<td>0.017</td>
</tr>
<tr>
<td>UO₂</td>
<td>0.024</td>
<td>0.031</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.002</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>28.61</td>
<td>1.01</td>
<td>0.12</td>
<td>0.05</td>
<td>42.34</td>
<td>0.43</td>
</tr>
<tr>
<td>F</td>
<td>0.65</td>
<td>0.05</td>
<td>0.24</td>
<td>0.05</td>
<td>3.86</td>
<td>0.37</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>SUM REO</td>
<td>70.034</td>
<td></td>
<td>22.467</td>
<td></td>
<td>0.252</td>
<td></td>
</tr>
</tbody>
</table>

At LTU, the general sample was sieved into fractions from 20 to 600 μm with sieve ratio 2, and the sieve fractions were sent for chemical analysis. The results did show that there was hardly any P₂O₅ in the fractions >300 μm, but approx. 30 % by weight <20 μm. The REE do mostly follow the P₂O₅ distribution, but do not have the same peak between 38-250 μm, and there is more REE in the fractions >300 μm. To further investigate, the correlation between P₂O₅ (apatite) and the REE, the mass and element distributions for all sieve fractions were subjected to Principal Component Analysis (PCA). A loadings (variable) plot (Figure 3) in the directions PC2 and PC3 shows that REE is correlated, but not totally, with the P₂O₅ distribution. In contrast, the correlation to Ca is strong and this implies that REE to a large extent substitutes for Ca. The conclusion is that REE in the Kiruna tailings pond is, besides in apatite, also present in some other Ca mineral, and that might be allanite or another REE-containing mineral.
Figure 2. Particle size distributions for samples and after grinding.

Based on a pre-study, the grinding time to freshen the mineral surface was locked at 10 minutes in a stainless steel rod mill (to not introduce colloidal iron). All flotation tests were run with a talc pre-float, to lower the Mg load, and an apatite rougher flotation followed by three cleaner stages. The tests were run with process water from Kiruna. This was sent to LTU in a 1 m³ tank and used in grinding, dilution after grinding, in flotation cells and as rinsing water in flotation.

A full factorial statistical test plan with three parameters was used: pH adjusted by NaOH solution, 9 – 11; Reagent (Collector) – Atrac 1563, 130 – 260 g/ton; Depressant – water glass, 500 – 1000 g/ton.

RESULTS

Flotation tests

The tests were evaluated with grade-recovery, selectivity curves, and difference indices for the main analyses. Product balances were calculated for all analyses, including individual REE, total REE, HREE and LREE. An example is given in Table 2 and Figures 4a-b. They show that it seems possible to achieve >30 % P₂O₅ in the concentrate with approx. 70 % recovery and fair selectivity towards MgO, SiO₂ and
Fe₂O₃. The selectivity diagram (Fig. 4b) also shows that REE is discharged in the rougher and the first cleaner stage. Heavy REE (Y, Eu to Lu) follows apatite better, but are also lost in the same way.

Figure 3. Multivariate loadings (variable) plot over mass and element distributions in the general sample

Table 2. Products balance for a good test; pH, collector, depressant – all low

<table>
<thead>
<tr>
<th>Product Notation</th>
<th>Mass (g)</th>
<th>Mass (%)</th>
<th>Product Mass Assays (%)</th>
<th>Assays (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc conc 1</td>
<td>42.9</td>
<td>4.3</td>
<td>SiO₂ 41.90</td>
<td>Al₂O₃ 5.00</td>
</tr>
<tr>
<td>Feed to flotation</td>
<td>965.8</td>
<td>95.7</td>
<td>CaO 10.80</td>
<td>Fe₂O₃ 13.20</td>
</tr>
<tr>
<td>Apatite conc 2</td>
<td>180.3</td>
<td>17.9</td>
<td>K₂O 1.17</td>
<td>Co 2.45</td>
</tr>
<tr>
<td>Cl-middl 3</td>
<td>35.7</td>
<td>3.5</td>
<td>MgO 1.84</td>
<td>Ba 0.37</td>
</tr>
<tr>
<td>Clean conc 2</td>
<td>152.3</td>
<td>15.1</td>
<td>MnO 3.36</td>
<td>V 0.37</td>
</tr>
<tr>
<td>Cl-middl 1</td>
<td>332.6</td>
<td>33.0</td>
<td>Na₂O 1.17</td>
<td>Cr 2.10</td>
</tr>
<tr>
<td>Rogher conc 2</td>
<td>633.2</td>
<td>62.8</td>
<td>P₂O₅ 1.17</td>
<td>TiO₂ 0.28</td>
</tr>
<tr>
<td>Tail</td>
<td>1008.7</td>
<td>100.0</td>
<td></td>
<td>247</td>
</tr>
</tbody>
</table>
Figure 4. a) grade-recovery and b) selectivity diagrams for a good test7

Response surfaces

To get a better view of how the parameters influence the responses, contour plots were made for recoveries of $P_2O_5$, REE and HREE, cf. Figures. 5a-5c. The overall view is that the best recoveries are for pH 9, high collector dosage and low water glass addition. Note that in all cases there is a local maximum for pH 11, high collector and high water glass. Therefore, the experimental space is 3-dimensional with a saddle point at the centre of the test series. It is interesting to note that said recoveries show the same general pattern. This indicates that the REE and HREE are either locked with apatite or in free-floting minerals with similar flotation properties as apatite.
DISCUSSIONS

The flotation results show that the best conditions for both apatite and REE winning are pH 9, high collector dosage (260 g/t) and low depressant addition (500 g/t). For this condition, laboratory scale flotation gives an apatite concentrate with 30 % P$_2$O$_5$ at 70 % recovery.

REE follows apatite in the cleaning, but not totally. The recovery of total REE to apatite concentrate is approx. half of that for apatite. For the heavy REE, it is slightly better. The final grade of REE in the flotation concentrate is fairly constant and related to the
$P_2O_5$ grade in the apatite concentrate. This implies that REE is not totally in apatite, and that there must be at least one unknown REE phase present. In later investigations it has been seen that a shorter grinding time leads to slightly higher REE recoveries, implying that a not so fine grinding gives better recoveries of liberated REE minerals.

When a full-scale recovering-dredging operation of the tailings pond is running during the winter, the feed to the concentrator will be just above freezing. Unfortunately, preliminary tests indicate unacceptable losses of apatite and REE when the flotation is run below 10 °C with the present reagent mix.

It appears that a large proportion of the REE is lost already in the rougher flotation and the first cleaner flotation. If this loss is caused by REE present in allanite, a test of the magnetic properties of the tailings might give some indication of the possibility to use high-gradient magnetic separation and/or amine based flotation to increase the total REE recovery.

**FUTURE WORK**

In the attempts to recover some of Europe’s most critical REEs from existing mine waste, it is fundamental to understand the occurrence of all REE containing minerals in the tailings and adapt flotation and other techniques to fit these specific minerals. This is one of the objectives in the recently started European project REEcover, where several European countries collaborate on finding new, and more efficient, techniques for characterization, analysis, extraction, and metal production of REEs.

As can be seen in the data presented in this paper, there is a need improving the accuracy of the characterization of REE-bearing minerals, and also on improving the detection of elements of very low concentrations, e.g. the HREE’s. To establish in detail the distribution and character of REE-bearing minerals with the purpose to develop the right extraction technique, quantitative analysis using Inca software will be performed on the Kiirunavaara material, as well as LA ICP MS analysis to be able to detect the absolute concentrations of REE’s in different mineral phases.

In a recent mineralogical survey by LKAB on an apatite concentrate, the mineral grades according to Table 3 were found. The mineral analyses come from Table 1. The calculated combined REO contents in mg/kg are compared with chemical analyses (ICP-MS) from flotation tests\(^7\). The two flotation tests gave nearly the same concentrate quality. The agreement between calculated and analysed contents is not so good, but what stands out is that chemically analysed Y grades are approx. five times higher than theoretically calculated. This indicates that the missing REE phase carries a relatively high Y content, and possibly other HREE’s.
Table 3. Comparison of REE-content in apatite concentrate

<table>
<thead>
<tr>
<th>Concentrate</th>
<th>Mineral Grade (%)</th>
<th>%SumREO</th>
<th>%La2O3</th>
<th>%Ce2O3</th>
<th>%Pr2O3</th>
<th>%Nd2O3</th>
<th>%Y2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apatite</td>
<td>70.65</td>
<td>0.252</td>
<td>0.020</td>
<td>0.200</td>
<td>0.027</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>Monazite</td>
<td>0.32</td>
<td>70.034</td>
<td>14.816</td>
<td>37.840</td>
<td>5.147</td>
<td>11.951</td>
<td>0.280</td>
</tr>
<tr>
<td>Allanite</td>
<td>0.40</td>
<td>22.467</td>
<td>6.989</td>
<td>11.442</td>
<td>1.271</td>
<td>2.466</td>
<td>0.319</td>
</tr>
</tbody>
</table>

Calculated concentrate grade contribution (mg/kg)

<table>
<thead>
<tr>
<th></th>
<th>SumREO</th>
<th>La2O3</th>
<th>Ce2O3</th>
<th>Pr2O3</th>
<th>Nd2O3</th>
<th>Y2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combined REO</td>
<td>4 920</td>
<td>895</td>
<td>3 084</td>
<td>216</td>
<td>669</td>
<td>122</td>
</tr>
<tr>
<td>N101:Test REE</td>
<td>3 550</td>
<td>608</td>
<td>1 290</td>
<td>164</td>
<td>603</td>
<td>472</td>
</tr>
<tr>
<td>N105:Test REE</td>
<td>3 484</td>
<td>617</td>
<td>1 250</td>
<td>161</td>
<td>587</td>
<td>486</td>
</tr>
</tbody>
</table>

Conversion REE/REO 0.8000 0.8527 0.8537 0.8545 0.8574 0.7874

Test equivalent bulk chemistry REO 4 396 718 1 488 190 694 608

Difference (Bulk-EMPA) eq REO -524 -177 -1 596 -25 25 487

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Application of modern methods for red mud processing to produce rare earth elements.

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Abstract

Nowadays red muds of the Ural refineries, wherein practically the whole content of scandium and the rare-earth elements content of bauxites is concentrated, are considered as one of the most promising raw sources of scandium in Russia. The paper contains a review and analysis of the methods of REE and scandium extraction from red mud known in the art to choose the most favorable one from ecological and economic point of view among methods/group of methods of REE and scandium extraction from this type of industrial wastes.

Introduction

Successful development of advanced engineering and technological industries is primarily determined by the use of new materials and products based on these materials. The use of scandium as an alloying additive in producing alloys makes it possible to produce materials with improved performance characteristics, that is, high strength, ductility, conductivity, etc. Another promising area of scandium application is the production of high temperature ceramics, phosphors, dielectrics, catalysts, refractories, etc. [1].

Currently, the red mud from Ural alumina refineries, in which almost all scandium and rare-earth metals contained in bauxite are concentrated, is regarded as one of the most promising sources of raw scandium in Russia. Most scandium and lanthanum contained in red mud is bound with iron and titanium minerals that undergo no changes in alumina production [2]. In addition to the high metal content (more than 100 g/t), red mud is completely prepared for further metallurgical processing, unlike other mineral formations. RUSAL's alumina refineries (UAZ and BAZ) annually stockpile about 2 million tonnes of red mud, which contains more than 200 tonnes of scandium. Notwithstanding the fact that scientists from around the world have been studying the problem of integrated red mud processing over the last 50-60 years, the least studied area, in our opinion, is that associated with the recovery of rare-earth elements and scandium from red mud. According to the results of a patent search conducted by Australian scientists from CSIRO, from 1964 to 2008, 135 patents were granted for
inventions in the field of red mud application in metallurgy, representing 17% of the total number of patents for red mud application (the patent analysis is based on the ISI Derwent Innovations Index data). A total of 10 patents, 2 and 8, respectively, were granted for the rare-earth metal and scandium recovery processes [3].

The purpose of this article is to summarise the information on the currently available methods of rare-earth metal and scandium recovery from red mud, as well as to select the most acceptable (from environmental and economic perspectives) method / group of methods for recovering rare-earth metals and scandium from these types of man-made materials.

The technologies for rare-earth metal recovery from red mud can be divided into two large groups: technologies based on the solid phase rare-earth metal pre-concentration methods followed by hydrometallurgical recovery of valuable components, and technologies for rare-earth metal digestion from the total volume of red mud. The first group of technologies includes such methods of rare-earth metal and scandium concentration as gravitational processing, magnetic separation, reduction roasting and reduction melting.

**Technologies for rare-earth metal recovery from red mud using rare-earth metal pre-concentration methods**

There are a number of studies by Soviet and Russian research teams related to the application of a combination of methods of classification, gravity concentration and magnetic separation to produce rare-earth metal and scandium concentrate. The red mud slurry was separated by density into sink and float. The sink (heavy fraction) was then subjected to magnetic separation with a magnetic field intensity of 40-160 kA/m to produce magnetic concentrate containing rare-earth elements, scandium and yttrium, which can be recovered by any of the existing methods. The magnetic concentrate produced was characterised by a low content of impurities, the recovery rate of rare-earth metal, scandium and yttrium was 50-60%, whereas there occurred no significant concentration of these elements as compared to their content in the initial red mud (no more than 1.5 times) [4].

The authors of the study [5] proposed a method for producing scandium-containing magnetic concentrate from red mud using the method of red mud slurry classification by particle size of 40-60 microns and further magnetic separation of fine impurities, with pH = 1.5-4.0 and magnetic field intensity ~ 30-80 kA/m. The magnetic concentrate yield was 4-7 % wt, the concentration of scandium in the concentrate was increased to 0.032-0.04 % wt compared to the scandium concentration in the initial red mud (0.01 % wt) [5]. There is also a method of scandium concentrate production using the combined methods of classification and magnetic separation, which consists in separating fine-grain fraction of red mud through classification, vibration cavitation
processing and further magnetic separation into magnetic and non-magnetic product. Under this method, the magnetic product was subjected to additional classification to produce iron-containing and scandium-containing concentrates with 0.040% Sc₂O₃. The concentrate yield was 5% of the initial red mud volume; the throughout recovery of scandium into concentrate – 19% [6]. The application of the methods above for pre-concentrating rare earth metals and scandium makes it possible to reduce the total volume of the solid phase targeted for digestion of valuable components (normally, acids). This results in reduced operating costs by minimisation of waste subject to disposal (acidic effluent, leaching cake, etc) as well as due to the process flow diagram simplicity. Notwithstanding the relatively low operating costs, these methods are characterised by a relatively low throughout recovery of scandium and rare-earth metals into the final product, as scandium recovery into the concentrate is less than 20%, and some part of scandium is lost in the process of sandium concentrate preparation into commercial scandium and rare-earth metal oxides. That is why their cost effectiveness is still questionable. It should be noted that the red mud particle size distribution has a strong influence on the technical and economic performance indicators of the magnetic separation method used in rare-earth metal concentrate production, in particular, for red mud resulting from processing bauxite from the Sredne-Timansky bauxite mine at UAZ, the average particle size is less than 10 microns, which precludes achieving the performance indicators specified in the studies [4-6]. The application of the pyrometallurgical methods of red mud processing for pre-concentration of the valuable components is based on the reduction bake out and reduction melting processes to produce iron and REEcontaining dross, which are separated using the magnetic separation method. Subsequently, the dross is sent for digestion of rare elements, i.e. rare-earth metals and scandium, the digestion agent being a 20-30% solution of H₂SO₄ [7-10]. The application of this group of methods results in a sharp increase in capital and operating costs (high energy consumption). Hence, the process of rare-earth metal and scandium recovery is economically inefficient.

**Technologies for rare-earth metal digesting from the total volume of red mud**

The second group of technologies for producing rare-earth metals and scandium from red mud includes a set of methods for digesting valuable components from the total volume of red mud, followed by further recovery from the solutions. This group of technologies can be divided into several subgroups depending on the type of digesting agents used for scandium recovery into solution: acid and carbonaceous digestion. The method of scandium carbonaceous digestion from red mud is based on the ability of scandium to dissolve and form anionic complexes, like (Sc(CO₃)ₙ)(2n-3)- (n≥2) over the
excessive hydrogen carbonates and carbonates of alkali elements [11]. The carbonaceous process of scandium recovery into solution, followed by its separation by hydrolysis or by sorption, is the most acceptable taking into account the specificity of the alumina production. At the same time, this process ensures a relatively low rate of scandium recovery into solution and does not allow simultaneous recovery of the rare-earth elements, the content of which in red mud exceeds 1 kg/t [12-15]. Thus, the problem of producing the combination of valuable elements (Sc, Ti, Zr, REM, etc.) contained in red mud in sufficiently high amounts can be solved using the acid digestion method only.

Based on the results of analysing literature data on the research in the given field conducted here and abroad, a conclusion was drawn regarding the most suitable digesting agents for recovery of rare-earth metals and scandium from red mud. Some of the most popular acid reagents for rare-earth metal and scandium recovery are sulfuric, hydrochloric and nitric acids. The bulk of studies are related to the use of diluted and concentrated sulfuric acid for digesting rare-earth metals and scandium both from red mud and magnetic concentrate, as well as dross, after reduction melting. The holders of the patent [16] propose a method for producing scandium-containing concentrate from red mud that includes the following stages: 1) digestion of scandium from red mud with 10.0-13.5% sulfuric acid with a preceding vibration cavitation treatment of slurry, duration − 15-35 minutes, process temperature − 30-95°C, 2) scandium sorption from sulfuric solutions on phosphoric ion exchangers, 3) wash down of the ion exchanger with a 1.0N HCl solution in order to remove titanium and zirconium impurities, 4) desorption of scandium with carbonaceous solution, and 5) sedimentation of scandium concentrate using sodium caprate. The relatively low acid concentration makes it possible to selectively recover scandium into solution, leaving most of the iron in the solid phase. The method makes it possible to achieve a 70-75.5% yield of scandium into the concentrate with its concentration in the final product − 22.5-25.0%. In the application [17], it is also proposed to treat red mud with a low concentration sulfuric acid (less than 10%) instead of using ineffective hydrochloric acid; scandium recovery into solution was 50%, yttrium recovery − 70%.

No data on recovery of other rare-earth metals into solution are given in the patent, no methods of scandium and yttrium recovery from solutions are specified. Russian scientists studied the process of red mud treatment by the methods used in processing low-quality uranium ores, that is: the method of rare-earth metal and scandium digestion with mineral acids, along with the ion exchange separation of radioactive and valuable components. Using the method of ion exchange in slurry with sulfuric acid, these scientists demonstrated the possibility of recovering titanium, scandium, uranium and thorium from the red mud at Nikolaev Alumina Refinery (Ukraine), where bauxites from Brazil, Guyana, Australia, Guinea and India are processed [18]. The advantages of using sulfuric acid for digesting processes over other reagents include but are not limited to low cost, the high level of knowledge related to the chemistry of
sulfate compounds, and the ease of the sulfate ion disposal by its binding into slightly soluble calcium sulphate.

Another popular reagent from the perspective of the research on rare-earth metal and scandium digestion from red mud is hydrochloric acid. Some researchers also suggest the successive use of hydrochloric acid and sulfuric acid solutions for scandium recovery from red mud [19]. To recover yttrium from red mud, there exists a widely known method for red mud treatment with a 5.7% solution of hydrochloric acid at a temperature of 85-95°C, where 70% of yttrium is recovered into the solution. This method implies a single-time or double circulation of the digesting solution in order to increase yttrium content in the solution up to 0.16 g/l. The resulting solution is subjected to further treatment using known methods for producing yttrium and its components [20]. Chinese researchers from the Taiwan University of Technology proposed a method for recovering scandium from modified red mud. This method includes the following stages: hydrochloric digesting of scandium, scandium recovery through extraction using composite extractant, and scandium concentrates sedimentation with oxalic acid [21, 22]. These same researchers suggest producing rare-earth metal concentrate by direct hydrolysis deposition from hydrochloric red mud digesting solution already silicon free [23].

Canadian researchers from Orbite Aluminae proposed a method of red mud complex processing to produce iron-bearing product, alumina and rare-earth metal concentrate [24]. This method includes the following stages: 1) Classification of aluminium-bearing material (50-80 micron fraction will be separated), 2) Treatment of the material with hydrochloric acid (with a concentration of 15-45%) making it possible, at a certain temperature and under certain pressure, to dissolve aluminium and other elements, such as iron, magnesium and other metals, including rare-earth elements and/or rare metals. Silicon dioxide and titanium remain completely in the solid phase; 3) Separation of the chloride solution from the solid residue; 4) Saturation of the acidic solution with dry high-concentration hydrogen chloride gas, which results in aluminum chloride hexahydrate crystallisation (sedimentation) with minimum concentration of other impurities; 5) Calcination of aluminium chloride hexahydrate at high temperature and production of alumina. The high-concentration hydrogen chloride released during calcination is passed through water to achieve even higher concentration, the final solution can be used at the digestion stage (recycling); 6) Ferrous chloride remaining in the solution is concentrated and hydrolysed at low temperature to produce Fe₂O₃ (a type of hematite), the acid being recovered during the process; 7) Treatment of the solution enriched with rare-earth elements and/or rare metals after hematite removal. Rare-earth elements and rare metals in the form of chloride are recovered from the solution using known methods such as the ultimate REM concentrate (e.g., liquid solvent extraction). To extract rare-earth metals, scandium and some other elements, it is suggested to use oxy-phenyl phosphoric acid and toluene, HCl is suggested to be used for re-extraction [24]. The main disadvantage
of the proposed technology is the complexity of the process of muriatic acid recirculation, which requires serious measures to be taken to create an airtight system for catching hydrogen chloride gas, as well as high capital expenses to ensure the corrosion resistance of the equipment in contact with gaseous HCl. Similar drawbacks hold true for the method of rare-earth metal recovery from red mud using SO₂ dissolved in water [25]. At the same time, the use of sulfuric acid makes it possible to selectively recover rare-earth metals into solution, leaving iron in the solid phase. The use of alkyl carboxylic acids as a digesting agent also makes it possible to recover selectively rare-earth elements into solution without extracting any significant amounts of iron into solution [26,27]. These technologies were trial tested on a pilot plant using sintering red mud from the Boksitogorsk Alumina Refinery. Particularly, the use of octanoic acid or the mix of synthetic fatty acids makes it possible to recover up to 30% of scandium and 9% of La into solution. The resulting organic phase containing rare-earth metals, aluminium and calcium was washed down with sulfuric acid solution (pH 3.0) in order to recover these elements into the aqueous phase, calcium precipitated from the solution as insoluble sulfate (gypsum), whereas rare-earth metals precipitated from the solution by way of its treatment with a 10% NaOH solution. Scandium was recovered from the organic phase after removing rare-earth metals, Al and Ca from it using sulfuric acid solution (pH 1.5) [26]. The same researchers suggested a method of rare-earth metal and scandium recovery from red mud involving the digestion of aluminium, calcium and rare-earth metals with formic or acetic acids. It was proven that the recovery rate of the target products depends significantly on the digestion time and temperature, i.e. the higher the temperature, the faster the maximum recovery rate of the following elements can be achieved: Al 50%, Ca 85%, Sc 63%, Yb 20%. The digestion solution was treated with sulfuric acid until the equilibrium value of pH 1.5 was reached in the aqueous phase, calcium in the form gypsum precipitated, formic acid was distilled from the filtered solution, the distillation residue was then treated with sodium carbonate solution, this resulted in rare-earth metals precipitating in the form of hydroxides, whereas aluminium and scandium remained in the solution as carbonates [27]. The distinctive feature of the last two methods of rare-earth metal recovery into solution using alkyl carboxylic acids is the necessity to use quite expensive reagents and formation of a large amount of gypsum at the acid regeneration stage.

Application of nitric acid for rare earth metals (REM) recovery from red mud was tested at the pilot unit, which makes it possible to feed 5 kg of red slurry at one time. The pilot unit was designed and manufactured in the NTUA Chemical Engineering Department laboratory (Athens, Greece) [28]. The designed technology includes selective recovery of scandium and REM to solution by red slurry digestion with diluted nitric acid solution; recovery of scandium and lanthanides using ion-exchange technique, and removal of diluted iron from their solution; further recovery of scandium by liquid extraction from eluate using di-(2-ethylhexyl) phosphoric acid, and
directing it to purification and concentration [29, 30]. The rate of scandium, yttrium and lanthanides recovery to solution reached 50-75 % depending on the element. Iron dissolution was insignificant. The acid capacity of a digesting agent was selected so that the scandium content could be increased in the solution at minimum dissolution of iron (< 4 %). The technology involves a process for nitric acid recycling. The limiting stage for the whole technology is digestion of scandium and REM from red mud. Therefore the pilot unit was manufactured in the NTUA laboratory.

The article [28] presents results of studies related to the following parameters' influence on digestion process: type of agitation, solid-to-liquid ratio, concentration of digesting agent, number of digestion stages, preliminary treatment of red slurry with concentrated acids for maximum scandium recovery at minimum dissolution of iron. The optimum conditions were selected for the scandium digestion process at a pilot production scale. The highest scandium concentrations in the solution were reached at the solid-to-liquid ratio increase, and media pH about 0. If pH increases, scandium concentration in the solution will reduce. The maximum rate of scandium recovery in the solution is 50 %, yttrium – 55 %. Behaviour of other REM during scandium recovery from red mud was not studied in this article.

Unfortunately, the authors did not consider the issues related to recycling red mud, and the environmental impact of the technology. Treatment of large volumes of red mud with nitric acid involves the need to recover the nitrate ions excess absorbed by red mud. As a result, large volumes of flushing water are produced. It is difficult to neutralise such flushing water. As opposed to sulphate ions, nitrate ions cannot form slightly soluble salts, and consequently, they cannot be removed using less expensive techniques. At the same time, maximum allowable concentration for nitrate ions (45 mg/l) is much lower than for sulphate ions (500 mg/l).

Having reviewed various technologies for REM and scandium recovery from red mud, we believe that, in terms of economic efficiency and advanced high-tech solutions for rare earth elements recovery and concentration, the most attractive option is the technology involving all stages of sulphuric-acid digestion of scandium and REM from red mud, scandium and REM sorption, and concentration of scandium and REM from the eluting solution.

Conclusion

At present there are many open issues related to selecting the most suitable technology for scandium and REM recovery from red mud of alumina production. In particular, most scientific studies lack information on specific REM behavior during red mud processing. These studies are mainly focused on scandium and yttrium recovery and related to the scientist’s assuming that all the rest of the elements are recovered with the same volume as yttrium. However, this fact is not proven by the results of the work [25, 26, 29, 30]. Besides, discussion of studies related to direct recovery of
scandium and REM from red mud does not cover the red mud recycling and environmental issues.
At the same time, it is obvious that digestion of scandium and REM from red mud should involve acid solutions with concentration making it possible to reach the highest REM recovery rate at minimum iron dissolution. Since digestion solutions contain insignificant volumes of scandium and REM, the most suitable technique for concentration is ion-exchange adsorption, which makes it possible to recover selectively REM and scandium using different types of ionites, or varying desorption conditions.

References

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HIGH PRESSURE ACID LEACHING OF A NICKEL LATERITE ORE TO EXTRACT SCANDIUM

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Abstract

The purpose of this experimental study on laboratory scale was to investigate the high pressure acid leaching (HPAL) behavior of the rare earth element scandium from a lateritic Ni-Co ore. In this work; the basic HPAL process parameters (sulfuric acid concentration, leaching temperature, leaching duration, and feed size) were studied and the optimum process conditions were determined to be as 260 kg sulfuric acid/ton of dry ore, 255 °C leaching temperature, 1 hour of leaching duration and 100% -850 μm feed size. Under these process conditions; 80.6% of scandium, 85.7% of nickel and 86.2% of cobalt could be extracted into the pregnant leach solution. In order to see the effect of finer feed size and longer leaching duration together, the ore was further ground to 100% -75 μm and leached for 360 minutes. It was seen that even under these extreme leaching conditions; only 84.7% of scandium, 88.7% of nickel and 90.6% of cobalt could be extracted. Thus; the present investigation has shown that the presence of chemically resistant minerals such as hematite and some clay minerals in the lateritic ore could be the possible reason for this incomplete dissolution behavior.

Introduction

Lateritic (oxide) and sulfide type nickel ores are the primary nickel and cobalt resources. Although most of the nickel has been supplied from the sulfide based resources since 1950’s, the trend in nickel production changed towards the more abundant laterite ores which constitute for about 70% of the world nickel resources. To confirm these remarks in the light of the historical data, it is seen that a small portion of (less than 10%) nickel was produced from lateritic sources in 1950’s. However, this ratio has increased up to ~42% in 2003, and rose up to ~50% in 2012. Moreover, it is forecasted that around 55-60% of nickel will be derived from lateritic sources in 2020’s [1-3]. In addition to nickel and cobalt, the presence of scandium has been detected in these resources and it seems that the importance of lateritic nickel ores will be more prominent in the near future. Since the supply of scandium is very scarce throughout the world, its field of application is limited for the time being and it is mainly used in the production of Al-Sc alloys, lighting, electronics, laser research and
solid oxide fuel cells (SOFC’s). However, it is believed that new application areas will emerge parallel to the increase in its supply.

Scandium is known to be present in many ore deposits and it was stated that the ores can be considered as worthy of exploitation if the scandium content ranges between 20 and 50 g/t [4]. Due to being widely dispersed, it is obtained during processing of various ores or tailings and residues from previously exploited mines as a by-product. In particular, it is obtained during processing of uranium, tin, tantalum, titanium, tungsten and rare-earth element sources and the major producer countries are China, Kazakhstan, Russia and Ukraine [5]. Due to its lack of affinity for the common ore forming anions, scandium is rarely concentrated in the Earth’s crust and generally found in more than 100 minerals in trace amounts in the form of solid solutions [5]. Due to the similarities in ionic radius, the most common substitution mechanism is the replacement of Fe\(^{3+}\) and Al\(^{3+}\) with Sc\(^{3+}\). Scandium in laterites is distributed widely among many minerals but may be especially associated with goethite, clay minerals or manganese oxides such as nickel-rich asbolane, in which it substitutes for Fe\(^{3+}\) and Al\(^{3+}\). Because scandium is distributed in much the same manner as nickel in lateritic ore minerals, it can be assumed that the leaching methods that solubilize nickel will also solubilize scandium. Some of the companies and research organizations working on leaching and recovery of scandium projects are: Jervois Mining Limited, EMC Metals Corp., Metallica Minerals, Sumitomo Metals Mining Company, Platina Resources, Pacific Metals Company and CSIRO.

Therefore, the aim of this study was to investigate the leaching behavior of rare earth metal scandium together with nickel and cobalt during high pressure sulfuric acid leaching (HPAL) of a lateritic ore. During this investigation, the basic process parameters (acid/ore ratio, leaching temperature, particle size, and leaching time) were studied and important findings have been presented in this paper.

**Experimental**

**Ore Sampling and Materials Characterization**

The sample was obtained from about 5000 tons of stockpile from Eskişehir/Yunusemre lateritic ore body located in Turkey. This representative sample was further split into suitable fractions by coning and quartering method. Initially the bulk and density measurements were performed. ‘Quantachrome Ultrapycnometer 1000’ helium gas pycnometer was used for its solid density determination. Multiple methods were used in chemical analyses during the study. Inductively Coupled Plasma (ICP) analyses were done by ‘Perkin Elmer DRC-II ICP-MS’ and ‘Perkin Elmer Optima 4300 DV ICP-OES’ devices. X-Ray Fluorescence (XRF) analyses were conducted using a 'Niton X-Met 820’ analyzer, and finally Atomic Absorption Spectroscopy (AAS) analyses were
performed by using ‘Perkin Elmer Analyst 400 AA’ analyzer. For mineralogical characterization, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Differential Thermal Analysis (DTA)-Thermo Gravimetric Analysis (TGA) methods were used. XRD measurements were done by a ’Rigaku Ultima-IV’ model X-Ray Diffractometer with a Cu-Kα X-ray tube working under 40 kV and 40 mA. Finally, the presence of minerals was verified with an ’FEI Nova Nano 430’ model scanning electron microscope.

**Experimental Set-up and Procedure**

High pressure sulfuric acid leaching experiments were performed in a 2 L, Parr-4532 titanium (grade-4) autoclave. To observe the leaching behavior; a slurry (150 g dried ore and 350 cc deionized water) of 30% solid content (excluding acid) were digested with 96-98 wt. % reagent grade sulfuric acid with a stirring speed of 400 rpm in all experiments. Because there was no direct acid injection system in the autoclave, sulfuric acid was added initially together with the ore slurry and the reactor was allowed to heat up to the desired leaching temperature in 40-45 minutes. The start of the reaction was defined as zero time when the reactor temperature reached to the set-point; subsequently, the leaching duration was recorded. After the completion of the reaction, the system was allowed to cool down to room temperature via water circulation system inside the reaction chamber. After digestion, the slurry was vacuum filtered in a Buchner funnel using a Whatman grade-4 filter paper for solid/liquid separation. Leach residue remaining on the filter paper was washed well with slightly acidic (pH 2) deionized water to clean the residue from the remaining pregnant leach solution fully without the precipitation of a portion of ions at higher pH. After washing, the leach residue was dried overnight at 105 °C and ground for chemical analyses. Meanwhile; the filtrate of the slurry was stored for chemical analyses, free acid determination, and oxidation-reduction potential (ORP) measurement. In order to measure the free acid remaining after digestion, the pregnant leach solution was titrated with 0.2 M sodium hydroxide (NaOH) solution. During titration, 280 g/L of reagent grade di-potassium oxalate monohydrate solution was used as a chelating agent to eliminate the interfering effect of some ions. Then, the residual acid was calculated from the amount of NaOH consumed via titration. For the oxidation-reduction potential measurements, a Pt-Ag/AgCl electrode (saturated with KCl) was used and the measured values were reported according to the Pt-Ag/AgCl reference electrode.
Results and discussion

Characterization Results
The as-received ore was found to contain about 14% moisture with the bulk and solid densities of 1.08 g/cm³ and 3.51 g/cm³, respectively. Chemical analysis of the representative lateritic ore sample is presented in Table 1.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Fe</th>
<th>Ni</th>
<th>Co</th>
<th>Sc (g/t)</th>
<th>Al₂O₃</th>
<th>MnO</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt. %)</td>
<td>46.2</td>
<td>1.54</td>
<td>0.093</td>
<td>106</td>
<td>3.61</td>
<td>1.04</td>
<td>0.71</td>
</tr>
<tr>
<td>Constituent</td>
<td>Cr₂O₃</td>
<td>SiO₂</td>
<td>CaO</td>
<td>Na₂O</td>
<td>K₂O</td>
<td>As</td>
<td>S</td>
</tr>
<tr>
<td>Content (wt. %)</td>
<td>2.25</td>
<td>14.56</td>
<td>0.98</td>
<td>0.02</td>
<td>0.02</td>
<td>0.12</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Mineralogical analysis of the sample was performed by XRD, SEM and DTA/TGA methods. XRD results given in Figure 1 showed that hematite (Fe₂O₃), quartz (SiO₂), and goethite (FeOOH) were the dominant mineral phases present in the ore. The presence of the goethite phase was also verified by DTA/TGA which exhibited a distinct endothermic peak between 260-340 °C according to the following dehydroxylation reaction

\[ 2\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \]

Additionally, minor amounts of nimite ((Ni,Mg,Fe++)₅Al(Si₃Al)O₁₀(OH)₈) and kaolinite (Al₂Si₂O₅(OH)₄) phases were also detected. Since, the peaks of these phases were small and dominated by the peaks of previously mentioned major ones; they were verified by separating clay and non-clay fractions and analyzing by XRD and SEM in detail.
Figure 1 XRD Patterns of the laterite ore sample and its HPAL leach residue

The SEM results also provided information regarding the other elements having no distinct mineral phases in the sample. According to the SEM results; nickel, chromium and manganese were found to be distributed substitutionally within the crystal structures of the iron oxides and the clay minerals (kaolinite, ninite). Similarly, cobalt was mainly found to be present in the crystal structure of clay minerals. However, there was no evidence for the distribution of scandium in the SEM results due to its relatively lower concentration in the sample. In order to interpret the distribution of scandium; the ore sample was separated into different size fractions (-850 +710, -710 +500, -500 +355, -355 +250, -250 +180, -180 +125, -125 +90, -90 +63, -63 +45 and -45 µm) by wet screening and each fraction was analyzed chemically. It was seen that there was a strong correlation in the distribution of scandium, iron and aluminum, which gave an indication about the presence of scandium within the crystal structures of the iron and clay minerals.

Extraction Results

Reliability of the experiments was controlled by repeating four analogous digestion tests with the same process parameters. The extraction results obtained from these tests are reported in Table 2.

Table 2 Reliability of HPAL experiments

<table>
<thead>
<tr>
<th>Element</th>
<th>HPAL-I</th>
<th>HPAL-II</th>
<th>HPAL-III</th>
<th>HPAL-IV</th>
<th>Mean</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni Ext.(%)</td>
<td>86.2</td>
<td>84.9</td>
<td>86.1</td>
<td>85.5</td>
<td>85.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Co Ext. (%)</td>
<td>86.7</td>
<td>86.9</td>
<td>85.6</td>
<td>85.7</td>
<td>86.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Sc Ext.(%)</td>
<td>81.5</td>
<td>79.9</td>
<td>80.9</td>
<td>80.1</td>
<td>80.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The experiments given in Table 2 were performed with the following process parameters; 255 °C leaching temperature with 0.260 acid/ore ratio for 60 minutes of leaching duration and -850 µm particle size. It is obvious from Table 2 that the nickel, cobalt and scandium extractions were sufficiently close to relying on the results of the experiments. Thus, the given parameters in Table 3 were tested, respectively.
Table 3 Studied process parameters during HPAL experiments

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Fixed Parameters</th>
<th>Studied Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric Acid/Ore Ratio (w/w)</td>
<td>255 °C, 60 min., -850 μm</td>
<td>0.16, 0.18, 0.20, 0.22, 0.24, 0.26, 0.27, 0.285, 0.30, 0.325, 0.35</td>
</tr>
<tr>
<td>Leaching Temp. (°C)</td>
<td>60 min., -850 μm, 0.260 acid/ore ratio</td>
<td>245, 255, 265, 275</td>
</tr>
<tr>
<td>Leaching Duration (min.)</td>
<td>255 °C, -850 μm, 0.260 acid/ore ratio</td>
<td>0, 30, 60, 90, 120, 360</td>
</tr>
<tr>
<td>Particle Size (μm)</td>
<td>255 °C, 60 min., 0.260 acid/ore ratio</td>
<td>-75, -425, -850</td>
</tr>
</tbody>
</table>

**Effect of Sulfuric Acid/Ore Ratio**
Initial the acid requirement was calculated according to the practical data of the operating plants and previously published studies [7, 8]. The first test was conducted with 160 kg of sulfuric acid per ton of dry ore and the highest amount of acid loading experiment was done with 350 kg of sulfuric acid. The effect of increasing acid load on the metal extractions can be seen in Figure 2.

![Figure 2](image)

**Figure 2** Effect of acid load on nickel, cobalt and scandium extractions
According to the data plotted in Figure 2, there was no significant change in the extraction of nickel. However; the cobalt extractions appeared to be adversely affected beyond 300 kg of acid per ton dry ore. In terms of scandium, the acid additions beyond 260 kg of acid per ton of dry ore led to a drastic decrease in the extraction of scandium. In order to understand this anomaly, the leach residues of the performed experiments were characterized and it was observed that a new iron sulfate hydrate phase (Fe₂O₃·2(SO₃)·H₂O) was formed due to excessive acid load as shown in Figure 3.

![Figure 3 XRD Patterns of leach residues w.r.t increasing acid concentration](image)

Similar precipitates were also observed at Moa Bay plant in the form of yellow balls at the point of acid injection in the first autoclave where zones of high acidity existed. Literature also supports this finding by stating that solids with sulfur contents similar to those of basic iron sulfate or jarosite form at free acid concentrations above a 'break-point', while a sulfur-deficient material (hematite) forms at acid concentrations below this break-point [9]. Since Sc³⁺ and Fe³⁺ have similar ionic radii, the available findings of the experiments indicated the possible precipitation of scandium together with iron sulfate hydrate due to higher acid loading. The previous mineralogical studies also indicated that Sc³⁺ substitutes for Fe³⁺ in the jarosite type structures due to similar reason [10]. Thus, the following HPAL tests were conducted with 260 kg of sulfuric acid per ton of dry lateritic ore.
Effect of Temperature
The positive effect of higher leaching temperatures during HPAL (in a limited temperature range) on nickel and cobalt extractions was reported in literature in the past. Generally, the leaching temperatures higher than 200 °C are selected due to higher nickel and cobalt extractions together with the dissolution and reprecipitation of iron, aluminum and some chromium at higher temperatures. These precipitation reactions provide cleaner pregnant leach solution for further processing and also decrease reagent consumption by regenerating the consumed acid at these temperatures. However, due to technical and economic reasons, higher leaching temperatures are limited up to around 275 °C. Moreover; the experimental studies reported the negative effect of increasing temperature beyond 270 °C due to co-precipitation of nickel in the newly formed precipitates such as \((\text{Mg,NI})\text{SO}_4\cdot\text{H}_2\text{O}\) [7]. Therefore; the temperature variation experiments were limited to the temperature range of 245-275 °C. The results of these experiments are given in Figure 4;

![Figure 4: Effect of leaching temperature on nickel, cobalt and scandium extractions](image)

According to the results plotted in Figure 4, it was observed that cobalt was unaffected from the temperature change. However, there was ~4% increase in the extraction of nickel with increasing leaching temperature. In terms of scandium, leaching temperatures higher than 255 °C led to a drastic decrease in the scandium extraction into the leach solution. To understand this unexpected observation, the XRD patterns of the experiments given in Figure 5 were investigated and it was seen that the formation of a new phase came into picture again as experienced in the acid load experiments.
Figure 5 XRD Patterns of leach residues w.r.t temperature

It was stated before by other workers in this field that leach temperature, acid/ore ratio and leaching duration have a significant effect on the sulfate content of the leach residue [11]. In particular, sulfur losses (i.e. solids sulfate content) are greater for higher leach temperatures and higher acid/ore ratios. The increase in sulfur content of the leach residue with temperature suggests the formation of a hydrolysis product with high sulfur content such as basic iron sulfates. To see this effect, the sulfur content of the leach residues were analyzed and it was seen that sulfur contents increased from 1.13% to 1.15%, then to 1.31% and finally to 1.70% with 10 °C increases in temperature from 245 °C to 275 °C, respectively. Thus, the remaining HPAL tests were conducted at 255 °C to determine the effect of the other parameters.

Effect of Particle Size and Leaching Duration

In the above mentioned work, the acid concentration and temperature were determined to be 260 kg acid/ton of dry ore and 255 °C within 60 minutes of digestion, respectively. However, the obtained extraction results were unsatisfactory since only 85.7% nickel, 86.2% cobalt and 80.6% scandium could be extracted into the pregnant leach solution with these parameters. Thus; in order to increase the metal extractions, finer particle size and higher leaching durations were tested. In industrial practice, the pressure leaching is generally conducted between 60-120 minutes. In order to study a broader range, the pressure leaching experiments were conducted between 0-360 minutes. According to the results presented in Figure 6 (left), it seems that the leaching was almost complete within the first 120 minutes of reaction and there was no effect of further leaching durations on the extraction of the desired metals.
Figure 6 Effect of leaching duration on nickel, cobalt and scandium extractions (left), Effect of particle size on nickel, cobalt and scandium extractions (right)

Since longer leaching durations did not give satisfactory result beyond 120 minutes, higher extraction efficiencies were tried to be obtained by finer particle size. Therefore; the ore used in the previous experiments (100% -850 µm) was further ground to 100% -425 µm and 100% -75 µm, respectively. As a result of grinding, only 2-3% increase was observed in the extraction yields of desired metals within 60 minutes as presented in Figure 6 (right). However; this increase was observed to be unsatisfactory due to over 10% un-reacted nickel, cobalt and scandium in the leach residue. Thus, to investigate an extreme case, the leaching duration of the finely ground ore (100% -75µm) was increased further from 60 minutes to 360 minutes. With these parameters ~3% increase in the nickel extraction and ~4% increases in the extractions of cobalt and scandium were observed.

In summary; even with the extreme leaching parameters (-75 µm particle size and 6 hours of leaching duration), approximately 10-15% of nickel, cobalt and scandium could not be extracted into the leach solution. To understand the possible reasons of these low extraction results, the XRD findings of the original sample and its leach residue obtained under the HPAL conditions of 260 kg sulfuric acid/ton of dry ore, 255 °C leaching temperature, 1 hour of leaching duration and 100% -850 µm particle size as given in Figure 1 were compared. According to Figure 1, it can be seen that almost all of goethite was leached and no remaining goethite phase was present in the leach residue. However, hematite and clay minerals were still present in the leach residue, which may be due to their incomplete dissolution during leaching. To support this finding, there are some reported studies referring to the difficulty in leaching hematite mineral [12, 13]. Therefore; undissolved primary hematite remaining in the leach residue may be one of the possible reasons of low metal extractions. In terms of clay minerals, it is known that these minerals are quite soluble during sulfuric acid leaching. However, in a previous study it was reported that kaolinite and clinochlore (chlorite
group clay member), similar to ninite, exhibited resistance to pressure acid leaching [14] and remained in the leach residue. According to the literature data, the dissolved iron species start to precipitate by ex-situ precipitation in solution on the primary hematite surfaces. This precipitation reaction was reported to begin within the first several minutes of leaching [11, 15, 16]. Thus, the precipitation of iron as hematite on the primary hematite particles could be one of the possible reasons of the un-reacted hematite mineral observed in the leach residue.

**Conclusions**

To test the extraction behavior of nickel, cobalt together with the rare earth metal scandium in a high pressure acid leaching process, the lateritic ore was digested by varying the following leach parameters: acid load, leaching temperature, leaching duration and particle size. In acid concentration experiments, it was seen that the excessive acid load beyond 260 kg/ton of dry ore led to the formation of iron sulfate hydrate precipitate and parallel to the formation of this precipitate, the scandium extractions decreased considerably. In terms of leaching temperature experiments, there was also a sign of sulfate formation and a decrease in the extraction values of scandium at higher leaching temperatures. The connection between the iron sulfate hydrate formation and decreasing scandium extractions was predicted to be due to simultaneous precipitation of scandium together with iron at higher acid loads and higher leaching temperatures due to similar ionic radii. Thus, the acid load and leaching temperature were selected to be 260 kg/ton dry ore and 255 °C, respectively. The leaching duration and particle size experiments indicated that 10-15% of nickel, cobalt and scandium could not be extracted into the leach solution even under the extreme leaching conditions (-75 µm particle size and 6 hours of leaching duration) at 255 °C and with 260 kg acid/ton dry ore. Thus, the possible cause of this behavior was investigated and it was decided to be due to incomplete dissolution of refractory minerals predicted to be as primary hematite and clay minerals.

**Acknowledgements**

The authors would like to express their special thanks to META Nikel Kobalt A.Ş. both for supplying the limonitic ore sample of Eskişehir/Yunusemre and for supporting the chemical analyses by XRF, AAS and ICP methods. In addition, the contributions of the METU Central Laboratory in ICP/MS/OES, DTA/TGA, and XRD analyses, the METU Metallurgical and Materials Engineering Department in SEM analyses and the SGS Ankara Geochem Lab. in ICP/OES analyses are gratefully acknowledged. The suggestions and support of MEAB Metallextraktion Company is also appreciated.
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References

LEACHING OF RARE EARTHS FROM BAUXITE RESIDUES USING IMIDAZOLOIUM BASED IONIC LIQUIDS.

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Abstract

Ionic liquids are versatile solvents that can be used as alternatives in the field of hydrometallurgy. At this study, a brief review of ionic liquids utilization in metal oxides and mineral leaching will be addressed followed by investigations for direct leaching of rare earth metals from synthetic REE oxides and metallurgical by-products. In particular, leaching of pure oxides of Lanthanum, Neodymium, Dysprosium and Yttrium and also Bauxite Residues (a solid residue generated from Bayer process in the primary aluminum industry), is investigated with pure ionic liquid 1-ethyl -3-methylimidazolium hydrogen sulfate (EmimHSO4/C2mimHSO4). Synthetic rare earth oxides totally dissolve in neat ionic liquid and high recoveries of rare earths and base metals were observed from bauxite residues.

Introduction

Ionic liquids (ILs) are ionic pairs which are liquid at ambient or low temperatures. Their properties include non-flammability, low vapor pressure, thermal stability, high conductivity and wide electrochemical window. Ionic liquids have been identified as alternatives to conventional solvents and are capable of enhancing the yield and selectivity of reactions [1]. Furthermore ILs are nonvolatile solvents in contrast with organic solvents and thus are safer to use in above ambient temperatures. They consist of an organic cation and an inorganic anion of different sizes (Fig. 1).

Figure 5 Chemical structure of 1-alkyl-3-methyl-imidazolium ionic liquid

Their properties play an important role as solvents for a number of applications like catalytic reactions [2-3] separation process [4-5] and electrochemistry [6]. IL’s can be used as design solvents or the so-called task specific ionic liquids, due to their ability to
adjust their physicochemical properties in a variety of applications. Thus hydrophobic or hydrophilic behavior can be monitored with modifying the number or the length of alkyl chains in the cation \[^4\] and also their miscibility with water by using different anions \[^2\]. Second generation ionic liquids that consist of 1-ethyl/butyl-3methyl-imidazolium cations with discrete inorganic anions are growing in interest for exploitation in mineral processing.

In this paper a review of the use of ionic liquids in mineral processing will be addressed and also the study of applying ionic liquid 1-ethyl-3-methyl-imidazolium hydrogen sulfate (EmimHSO4) as leaching medium for rare earth oxides will be presented.

**Dissolution of metal oxides using ionic liquids**

The first reported studies of leaching metal oxides in ionic liquids concerned the dissolution of UO\(_3\) and V\(_2\)O\(_5\) in imidazolium chloroaluminate melt\[^7\-\^8\]. The solubility of UO\(_3\) was found to be 1.5-2.5 \(10^{-2}\) mol/dm\(^3\) and the main species in solution was [UO\(_2\)Cl\(_4\)]\(^2-\). Vanadium oxide was found to be very soluble in the basic melt, 0.15 g in 1 g, but also soluble in the neutral melt. Task specific ionic liquids are ionic liquids designed for specific purposes such as betaine bis(trifluoromethylsulfonyl)imide\[^9\](HbetTf\(_2\)N), which have been used for the dissolution of the rare earth oxides; imidazolium, pyridinium, pyrrolidinium, piperidinium, morpholinium, and quaternary ammonium bis(trifluoromethylsulfonyl)imide salts were also functionalized with a carboxyl group for the selective dissolution of metal oxides and hydroxides \[^10\]. Oxides such as rare earth oxides, UO\(_3\), PbO, ZnO, CdO, HgO, CuO, Ag\(_2\)O, NiO, PdO as well as several hydroxides were soluble in these ionic liquids whereas Co oxides, Cr\(_2\)O\(_3\), FeO, Fe\(_3\)O\(_4\) found to be insoluble in the same experimental conditions.

Deep eutectic solvents of choline chloride mixtures with hydrogen bond donors such as carboxylic acids, amines and alcohols have been studied for dissolving metal oxides \[^11\-\^15\]. The solubilities of ZnO, CuO, and Fe\(_3\)O\(_4\) have been determined in 3 deep eutectic solvents between choline chloride and carboxylic acids at 50°C \[^12\]. Fe\(_3\)O\(_4\) is more soluble in oxalic acid/ChCl system whereas 20 times less soluble in phenylpropionic acid mixture while CuO showed the opposite behavior, suggesting that deep eutectic solvents can be applied for selectively leaching of metals. In addition the solubility of 17 common metal oxides have been determined in ionic liquids of choline chloride mixtures with urea, malonic acid, and ethylene glycol \[^13\]. At present the behavior of rare earth oxides in such deep eutectic solvents have not been studied.

The dissolution of Ca, Ni, Mn, Co, Cu, and Zn oxides in hydrophobic ionic liquid trihexyl (tetradeccyl) phosphonium chloride (Cyphos IL 101) saturated with a concentrated aqueous hydrochloric acid solution have been also investigated \[^16\]. Here the IL works as in solvent extraction, as the dissolved oxides can be in subsequent step recovered in an aqueous phase through selective stripping.

A summary of ionic liquids reported for metal oxide dissolution is shown table 1.
Table 4 Dissolving metal oxides in ionic liquids

<table>
<thead>
<tr>
<th>Ionic liquid/leaching agent</th>
<th>Metal oxides studied</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EmimCl/AlCl₃</td>
<td>Uranium- Vanadium</td>
<td>7,8</td>
</tr>
<tr>
<td>DMPIC/AlCl₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HbetTF2N, [C₆Hbet]TF2N, [C₄Hbet]TF2N, [HbetmIm]TF2N, [HbetmPyr]TF2N, [EtHbetmMor]TF2N,[HbetmMor]TF2N, [HbetmPip]TF2N, ([HbetmPyr]-TF2N),</td>
<td>Sc, Y, La, Pr, Nd,Sm, Eu, Gd, Tb, Dy, Ho, Er,Tm,Yb, Lu, U, Pb, Zn, Cd, Hg, Cu, Ag, Ni, Pd, Mn, Co, Cr, Fe, Al and Si</td>
<td>9,10</td>
</tr>
<tr>
<td>[Deep eutectic solvents] Choline chloride/urea/ethylene glycol/malic acid</td>
<td>Ti, V, Cr, Mn, Fe, Co, Al, Si, Ca, Cu, Ni, Pb and Zn</td>
<td>13</td>
</tr>
<tr>
<td>(Cyphos IL 101-saturated with concentrated hydrochloric acid)</td>
<td>Ca, Ni, Mn, Co, Cu, and Zn</td>
<td>16</td>
</tr>
<tr>
<td>Emim(X−), X= (Cl−), (SCN−), (DCA−), (OAc−), (Tf2N−)</td>
<td>Ag, Cu, Ni and Zn</td>
<td>17</td>
</tr>
</tbody>
</table>

Ore and wastes processing with ionic liquids

Few studies have dealt also with processing ores and wastes with ILs for leaching valuable metal oxides. 

Electric arc furnace dust: Choline chloride with urea has been applied for processing electric arc furnace dust \[14,15\]. EAF dust consist mainly of metal oxides. Urea mixture had been chosen due to the low solubility of iron oxide towards high solubility of ZnO and CuO in it. Leaching of EAF with 2:1 molar ratio ChCl/urea conducted at 60°C for 48h. ZnO, Cu₂O and PbO can be selectively leached and subsequently recovered from the liquid through cathodic electro-deposition. A pilot plant with a capacity of 5kg dust batches has already been built.

Brass ash: BmimHSO₄ has been investigated for leaching of industrial brass ash in order to recover copper and zinc. Parameters such as dissolution time, IL concentration and oxidizing agents have been studied \[16\]. 99% dissolution efficiency has been achieved for Zn and 24.82% for Cu after 4h of leaching at 70°C with 50% v/v BmimHSO₄ in water. To increase the extraction ratio of Cu oxidizing agents were added to the leaching solution. With H₂O₂ addition up to 82% of Cu was leached at 70°C after 5h.

Sulphidic ores containing gold and silver: The first reported study of BmimHSO₄ utilization in metal leaching concerned the extraction of Au and Ag from a complex gold bearing ore \[19\]. The leach solution was prepared by dissolving thiourea in BmimHSO₄ in the presence of Fe₂(SO₄)₃. Leaching was carried out at 50°C resulting in 85% Au recovery and 60% Ag recovery. The remaining base metals copper, lead, zinc and iron had low extraction yields. Furthermore recycling of BmimHSO₄ has been
studied by stripping the leach liquor with activated carbon. Altering IL organic cation while maintaining the HSO₄⁻ anion revealed that as the alkyl chain of the alkyl-methylimidazolium hydrogen sulphate increases from butyl to octyl, the extraction of gold decreases. This may be attributed to the corresponding rise of the viscosity of the IL solution. Except from the cation alteration, different anions have been studied keeping the butyl chain of the cation constant. BmimCl, BmimBF₄, BmimN(CN)₂ and BmimCH₃SO₃ were studied for gold extraction. Significant recoveries occur for the BmimCH₃SO₃ and BmimHSO₄ for gold, silver and base metals. Moderate recoveries occur for BmimBF₄ and low recoveries for BmimN(CN)₂ and BmimCl. These observations suggest that the anion in the ionic liquid plays an active role during the dissolution process. Furthermore leaching of gold and silver was studied in the presence of (peroxomonosulfate HSO₅⁻) or Fe(III) oxidants, and complexing agents such as thiourea, Cl⁻, Br⁻ and I⁻ using BmimHSO₄ and BmimCl as solvent medium. Over 85% of gold was leached and significant amount of silver recovered in the presence of HSO₅⁻/thiourea at 25–50 °C in both BmimHSO₄ and BmimCl. HSO₅⁻/thiourea system had the same leaching efficiency as the Fe(III) thiourea system. Recoveries of gold and silver were significantly higher than in an aqueous medium and negligible recoveries of base metals obtained in ionic liquids.

**Chalcopyrite:** Chalcopyrite leaching was studied with 1:1 water: Bmim(BF₄) volume ratio in the presence of Fe(BF₄)₃. 90% of copper extraction was achieved after 8 h at 100 °C. BmimHSO₄ and its aqueous solution were used for leaching chalcopyrite in temperature range from 50 to 90°C. Copper extraction increased from 52% to 88% as ionic liquid concentration increased from 10% to 100% at 70°C for 24h. 1-alkyl-3-methyl-imidazolium ionic liquids were studied as solvent medium either in neat or in aqueous mixtures, in the presence of thiourea and iron (III) as an oxidant. Initially the leaching behavior of pure pyrite was studied in pure BmimHSO₄, leading to poor results. Chalcopyrite ore concentrate behaved differently during its leaching in the same medium. 85% recovery of copper and less than 8% iron dissolution were achieved after leaching of chalcopyrite at 60°C with 20%w/v in water. The metal extraction increases with temperature. Moreover increasing the concentration of BmimHSO₄ also lead to higher extraction yields for copper. In comparison to leaching the same chalcopyrite ore concentrate with an aqueous 1M H₂SO₄ solution, the abovementioned BmimHSO₄ solution achieves 62% higher Cu leaching efficiency. A summary of the research works that have studied the use of ionic liquids as solvents in mineral processing can be seen in Table 2.
Table 5 Ionic liquids in mineral processing

<table>
<thead>
<tr>
<th>Ionic liquid/leaching agent</th>
<th>Minerals</th>
<th>Target Metals</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Deep eutectic solvents] Choline chloride:urea</td>
<td>Electric arc furnace dust (oxidic form)</td>
<td>Zn, Cu, Pb</td>
<td>14,15</td>
</tr>
<tr>
<td>BmimHSO₄/H₂O₂ or potassium peroxymonosulfate</td>
<td>Industrial brass ash (oxidic form)</td>
<td>Zn, Cu</td>
<td>18</td>
</tr>
<tr>
<td>BmimHSO₄/thiourea and Fe₂(SO₄)₃</td>
<td>sulphidic ores containing Au,Ag</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>Bmim‘X’, (X = Cl⁻, CH₃SO₃⁻, N(CN)₂⁻, BF₄⁻, HSO₄⁻)/thiourea and Fe₂(SO₄)₃</td>
<td>sulphidic ores containing Au,Ag / pyrite, sphalerite chalcopyrite</td>
<td>Au, Ag</td>
<td>20</td>
</tr>
<tr>
<td>BmimHSO₄ or BmimCl/peroxymonosulfate (HSO₅⁻) or iron (III), and complexing agents thiourea, chloride, bromide and iodine</td>
<td>sulphidic ores containing Au,Ag</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>Fe(BF₄)₃ in water:Bmim(BF₄) at 1:1</td>
<td>chalcopyrite</td>
<td>Cu</td>
<td>22</td>
</tr>
<tr>
<td>BmimHSO₄</td>
<td></td>
<td></td>
<td>23</td>
</tr>
</tbody>
</table>

Leaching rare earth oxides using ionic liquids

This study will present preliminary results for utilizing ILs in leaching Rare Earth oxides from both synthetic oxides and REE containing metallurgical wastes. **Synthetic rare earth oxides**: Preliminary experiments investigated the dissolution behavior of synthetic rare earth oxides in neat IL EmimHSO₄. Ionic liquid EmimHSO₄ with purity 95% was obtained from Sigma Aldrich and was used without any further purification. The oxides studied were yttrium oxide, neodymium oxide, dysprosium oxide and lanthanum oxide which were obtained from Alfa Aesar with 99.9% purity.
The experiments were conducted by introducing 1g of dried rare earth oxide powder into 10ml of pure ionic liquid (10% w/v pulp density). Temperatures were varied from 90 to 210°C, where EmimHSO₄ remains stable and liquid. The end point of the leaching experiments was determined by optical observation (fig. 2), at the point where a clear solution was obtained. The hot solution was then filtered using fiber glass filters and the resulting filter paper washed with deionized water. Atomic absorption spectroscopy was used to measure the metal content in the pregnant solution and thus to determine the total dissolution of the REE oxide. The time needed to achieve the complete dissolution of different rare earth oxides under different temperature is shown in figure 3.

![Figure 6](image1)

**Figure 6** Neodymium (left) and Lanthanum (right) oxide dissolving in neat EmimHSO₄ at elevated temperatures. The solution becomes clear in less than 5 minutes at 210°C.

![Figure 7](image2)

**Figure 7** Time needed for total dissolution of 1 g of various rare earth oxides in 10 ml of neat EmimHSO₄ at different temperatures.

At elevated temperature rare earth oxides dissolve in very short times. At lower temperature lanthanum and yttrium oxide didn’t dissolve and their solution formed a highly viscous gel-like phase. The trend here shows that dissolution is highly effected with temperature, which can be related to the significant decrease in the viscosity of EmimHSO₄, shown in table 3, leading to better wettability of the solids and faster dissolution rates.
### Table 6: Viscosity of neat EmimHSO₄ at different temperatures \(^{[24]}\)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>20 °C</th>
<th>100 °C</th>
<th>150 °C</th>
<th>200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (mPa·s)</td>
<td>1354</td>
<td>55</td>
<td>13</td>
<td>4</td>
</tr>
</tbody>
</table>

**Bauxite residue (red mud):** Bauxite Residue, also known as red mud, is the major solid waste generated during the primary alumina production with the Bayer process. For each tone of alumina produced, almost 1 tone of residue is generated. This amounts to approximately 120 million tons of bauxite residues that are produced worldwide each year. Significant research effort takes place for the effective utilization of Bauxite Residues \(^{[25-27]}\), while its potential as a source for REE production has also been proposed \(^{[28-30]}\).

In the present study bauxite residues provided by ALSA S.A in Greece were used. Chemical analysis of the sample was performed after total dissolution with a fusion method and rare earth elements were measured using inductively coupled plasma mass spectroscopy (ICP-MS) while base metals with atomic absorption spectroscopy (AAS). Calcium and sodium were determined with XRF method. The results are presented in Table 4.

**Table 7: Chemical analysis of ALSA’s Bauxite residues sample**

<table>
<thead>
<tr>
<th>Red mud oxides</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>TiO₂</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>REO</th>
<th>Loss of ignition %wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical analysis %wt.</td>
<td>43%</td>
<td>25%</td>
<td>9%</td>
<td>5%</td>
<td>5%</td>
<td>2%</td>
<td>0.14%</td>
<td>10%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rare earths in Bauxite Residues (mg/Kg)</th>
<th>Ce</th>
<th>Pr</th>
<th>La</th>
<th>Sm</th>
<th>Sc</th>
<th>Dy</th>
<th>Sm</th>
<th>Gd</th>
<th>Er</th>
<th>Yb</th>
<th>Y</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>512</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>193</td>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>135</td>
<td>24</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>Nd</td>
<td>129</td>
<td>21</td>
<td></td>
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<td></td>
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<tr>
<td>Y</td>
<td>114</td>
<td>13</td>
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<tr>
<td>Er</td>
<td>13</td>
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<td></td>
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</tbody>
</table>

Scandium oxide is 0.02% wt. in the red mud analyzed, a concentration considered to be exploitable \(^{[30]}\). Overall the REE concentration in the ALSA red mud is in the same levels of concentrations reported in previous studies \(^{[31]}\).

Minerals that have been identified by XRD in red mud are mainly hematite [Fe₂O₃], gibbsite [Al₂O₃·3H₂O], diaspore [Al₂O₃·H₂O], cancrite [Na₆Ca₂(Al₆Si₆O₂₆)(CO₃)₂], katoite [Ca₃Al₂(SiO₄)(OH)₈] and rutile [TiO₂]. Measurements on grain size distribution indicate an average grain size of 12 μm.

Direct leaching of red mud with EmimHSO₄ at different pulp densities was contacted at elevated temperatures. After 24h of leaching at 190°C, filtration at high temperatures and washing the resulting filter cake with deionized water the filtrate
was analyzed in ICP-MS and AAS. Experiments at 5% and 2.5% pulp density (w/v) were carried out. The metal recoveries are shown in figure 4.

![Figure 8](image)

**Figure 8** Recovery of rare earths and base metals from red mud after leaching with neat EmimHSO4 at 190 °C for 24h.

At these leaching conditions almost total dissolution of iron and titanium was observed while the residue consisted mainly of aluminum and silicon. EmimHSO4 showed no particular leaching selectivity between rare earths and base metals. The average recovery yield of rare earths increased with decreasing pulp density, reaching a 60-70% at the 2.5% pulp density. The resulting concentration of the pregnant leach solution is given in table 5.

**Table 5** Concentration of metals in EmimHSO4 after leaching bauxite residue (2.5% w/v pulp density at 190°C, 24h).

<table>
<thead>
<tr>
<th>Elements</th>
<th>% recovery</th>
<th>~mg/L solvent</th>
<th>Elements</th>
<th>% recovery</th>
<th>~mg/L solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>100</td>
<td>5</td>
<td>Al</td>
<td>36</td>
<td>1205</td>
</tr>
<tr>
<td>Nd</td>
<td>70</td>
<td>2</td>
<td>Fe</td>
<td>100</td>
<td>7650</td>
</tr>
<tr>
<td>Y</td>
<td>61</td>
<td>2</td>
<td>Ca</td>
<td>39</td>
<td>627</td>
</tr>
<tr>
<td>Ce</td>
<td>70</td>
<td>9</td>
<td>Na</td>
<td>86</td>
<td>318</td>
</tr>
<tr>
<td>Sc</td>
<td>68</td>
<td>2</td>
<td>Ti</td>
<td>100</td>
<td>700</td>
</tr>
</tbody>
</table>

**Kinetic experiments:**
Keeping temperature constant at 190°C and pulp density at 2.5%(w/v), kinetic experiments were conducted with neat EmimHSO4 for ½, 2, 6, 8, and 24h. The metal recoveries are shown in figure 5.
Figure 9 Recoveries of selected metals versus time after leaching with EmimHSO4 at 190 °C for ½, 2, 6, 8, 24 h.

After 2 hours retention time high recoveries for Fe and Ti were achieved. Iron is totally recovered within the first 2 hours of leaching. Titanium is dissolved fast during the first two hours, reaching a recovery of 80% and then its leaching rate is decelerated necessitating 24 hours retention time in order to achieve 100% recovery. Scandium (as a proxy for all REE) reaches also almost it’s maximum recovery in 2 hours and prolonging the leaching time does not seem to have a significant effect as in the case of Ti leaching. Aluminum follows a very slow dissolution process and its recovery doesn’t exceed 35% after 24 hours retention time.

Effect of altering the alkyl chain in 1-alkyl-3methyl-imidazolium hydrogen sulfate:

Altering the alkyl chain in imidazolium cation by using the ionic liquids 1-butyl-3methyl-imidazolium hydrogen sulfate (BmimHSO4 >95% purity), and 1-methylimidazolium hydrogen sulfate (HmimHSO4 >95% purity) resulted to small differences on metal recoveries from Bauxite residues as seen in figure 6.

Separating the metals in three different groups, it can be concluded that base elements reach their maximum recovery in EmimHSO4 while Na and Ca follow an opposite trend.
Rare earth elements such as La, Nd and Ce present their lowest recoveries in BmimHSO4 whereas Sc recovery is practically unaffected by the alteration of cations. Overall small changes occur with the variation of the IL cation.

**Preliminary results with task specific ILs:** Despite the high recoveries of rare earths achieved with the imidazolium - hydrogen sulfate ILs, the pregnant solutions produced contain large amounts of dissolved Fe and Ti, making the extraction of the REE from such solutions impractical. Thus future investigations should be focused to exploit ionic liquids for selective dissolution between critical metals and iron as the latter is the most abundant in red mud. As an indication for this potential, in figure 7 the results of a preliminary leaching test of Bauxite Residue with the task specific IL betaine bis(trifluoromethylsulfonyl)imide (HbetTf2N) is shown. The results indicate that the specific IL favours the dissolution of Ca, Na, REE and other minor elements while the iron of the Bauxite Residue remains practically undissolved.

![Figure 7](image_url)

**Figure 7** Direct leaching of red mud with 50% v/v HbetTf2N in water at 60 C with 10%pulp density for 24h.

**Conclusions**

In the present study direct dissolution of synthetic rare earth oxides and red mud has been made with ionic liquid EmimHSO4. Preliminary experiments with pure ionic liquid EmimHSO4 and synthetic rare earth oxides prove that dissolution process is feasible and occur at shorter times as temperature rises. Neat EmimHSO4 provides the acidity needed for the metal oxides to dissolve and form metal complexes as other studies with imidazolium ionic liquids proposed [17]. Bauxite residue also dissolve in EmimHSO4. Small dissolution of silicon and aluminum occur and high recoveries of rare earth elements such as yttrium, lanthanum, cerium, neodymium and scandium have been obtained in the range of 60-70%. Alteration of the cation in imidazolium hydrogen sulfate ionic liquid has little effect in the metals recovery. Preliminary results show that utilizing different ILs, such as the HbetTf2N may even achieve selective leaching of the REEs. Thus from these studies and literature investigations ionic liquids seem to be promising alternative solvents for primary and secondary raw materials processing.
Acknowledgments

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Session VI-A: REE Processing-REE Separation
FUNCTIONALISED MIL-101(Cr) AS NOVEL EUROPIUM ADSORBENT

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Abstract

In this contribution we report the synthesis of a novel MOF-based adsorbent for europium. MIL-101(Cr) is functionalised in a stepwise manner to create a material bearing carbamoylmethylphosphine oxide (CMPO) ligands, which are selective towards lanthanide complexation. Analysis showed that the adsorbent contains $\approx 0.7$ mmol of CMPO ligands per gram. Preliminary adsorption capacity tests have been performed resulting in a capacity of $\approx 17$ mg Eu/g adsorbent.

Introduction

The rare earth elements (REEs), a group of valuable metals, are gaining an ever-increasing importance to our modern society. Mainly consisting of the fifteen lanthanides, these rare earth metals are found in a variety of high-tech applications. Especially in the field of clean energy, many of the lanthanides (e.g., neodymium, dysprosium, europium,...) play a critical role in the design and operation of appliances and machinery such as wind turbines, hybrid and electrical vehicles and lighting technology\textsuperscript{1}. With China currently controlling about 97\% of the rare earth production, only a fraction of the mined metals reaches the international market as export product\textsuperscript{2}. Opposite to this limited supply stands a rapidly increasing demand that is unlikely to decelerate. Maintaining the rare earth supply will be crucial to a technologically sustainable future. One important way to achieve this goal is to anticipate on rare earth recycling. In this contribution we allude to one specific part in the complex chain of recycling processes, namely the recovery of rare earth metals from dilute aqueous streams.

Many metal recycling processes (and also primary mining processes, for that matter) end up with acidic solutions in which various metals are present in their dissolved ionic form. The current state-of-the-art (rare earth) recovery techniques consist of sequential liquid-liquid extractions or precipitation processes to selectively separate the valuable metals from any unwanted species\textsuperscript{3}. While these techniques have proven their worth in terms of selectivity, their recuperation yield is not 100 \%. Typically, these techniques generate aqueous waste streams containing several hundreds of milligrams of rare earth metals per litre. In the past decade it was not necessary, nor
was it economically feasible to recover these small amounts of rare earths. But with their increasing scarceness, the incentive has become far greater to expand industrial recovery to these streams as well.

An efficient and cost-effective way to remove and/or recover specific species from dilute solutions is adsorption. Being a heterogeneous process, adsorption has the advantage of easy separation and reuse. An adsorbent for rare earth metals, however, must meet several requirements. First of all, the adsorbent needs to interact selectively with the rare earth cations. This implies the embedding of specific functionalities into the adsorbent support, which neglect unwanted cations (transition metals, alkali metals,...) as much as possible, if not completely. Another important property is adsorbent stability. Not only does the support material have to perfectly survive the acidic aqueous conditions during the adsorption and regeneration, also the linkage between support and the immobilised functionality requires the proper stability to prevent leaching and to promote reuse of the adsorbent.

In this study, metal-organic-frameworks (MOFs) are introduced as a novel support in the field of liquid adsorption. More specifically the chromium based MIL-101 was functionalised and applied as selective adsorbent for europium. MIL-101(Cr) is a type of mesoporous cage-MOF, introduced in 2005 by Ferey et al.\textsuperscript{4}. Its three-dimensional framework is made up of inorganic chromium-oxide clusters connected via terephthalate linkers, forming cages of super tetrahedra (Figure 1). The presence of the aromatic linkers makes post-functionalization of the MOF particularly easy. The MIL-101(Cr) is amongst the most stable mesoporous MOFs to date, possessing excellent resistance to acidic aqueous media\textsuperscript{5,6}. Furthermore, it is a highly porous MOF, where the mesoporous cages permit the incorporation of spacious molecules.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) MIL-101(Cr) super tetrahedron. (b) Small super cage. (c) Large super cage. (d) MIL-101 MTN zeotype structure.}
\end{figure}

All of the lanthanides form trivalent cations and as a general rule, these cations tend to be fairly hard Lewis acids as a result of their high oxidation states. Therefore, when designing a ligand field to selectively bind the lanthanide cations, it is advisable to incorporate hard Lewis bases into the ligand structure (cfr. the HSAB concept). In addition, an interesting phenomenon arises with these cations, in which the binding of one class of ligands to the cation enhances the affinity of another class of ligands. This results in a very selective complexing behaviour\textsuperscript{7,9}. For the rare earth cations, the most important types of synergistic ligands are the amide carbonyl group and...
phosphine oxide based ligands. A very efficient system based on the aforementioned ligand combination is the so-called CMPO ligand (carbamoylmethylphosphine oxide, Figure 2). These ligands are known to be very selective towards lanthanide complexation, while having little to no affinity for ordinary transition- or alkali metals.

![Figure 2: Carbamoylmethylphosphine oxide (CMPO) ligand structure.](image)

By heterogenising these kinds of ligands, one can create a selective adsorbent for rare earth elements. In this on-going research, we aim to develop a selective adsorbent based on the MIL-101 as solid support. This is performed by a step-wise build-up of the ligand onto the MOF support. The materials are tested in the adsorption of europium from aqueous solutions. In these preliminary tests, we investigate the europium retention capacity of these developed adsorbents.

**Experimental**

**Chemicals**

Europium(III) oxide (99.9 %) was purchased from Alfa Aesar. Europium standard solution (1,000 mg/l Eu\(^{3+}\) in dil. nitric acid) was purchased from VWR Chemicals. All other chemicals were purchased from Sigma Aldrich.

**Synthesis of MIL-101(Cr)**

MIL-101(Cr) was synthesized based on an adapted recipe from Jiang et al. In a typical experiment, terephthalic acid (0.665 g, 4 mmol) and Cr(NO\(_3\))\(_3\)-9H\(_2\)O (1.608 g, 4 mmol) were added to deionised water (20 ml). The resulting suspension was added to a Teflon-lined autoclave and subjected to 210 °C during 8 hours under autogenous pressure (2 hours warm-up). After cooling down to room temperature, the mixture was filtered and the solid green product was collected and washed thoroughly with dimethylformamide (DMF) and water in order to purify the material by removing any unreacted reagents. Samples were vacuum dried at 120 °C for 24 hours.

**Characterization**

Nitrogen gas sorption experiments were conducted at 77 K with a Micromeritics Tristar 3000. Samples were vacuum dried at 120°C prior to analysis. The specific surface area was calculated using the Langmuir method. DRIFTS-spectra were measured on a Nicolet 6700 FTIR spectrometer (Thermo-Scientific) with an MCT detector. Analyses were performed at 120 °C under vacuum. X-ray fluorescence (XRF) spectroscopy measurements were performed on an energy-dispersive Rigaku NexCG spectrometer. Elemental analysis (CHNS) was performed on a Flash 2000 (Thermo-Scientific). Powder X-ray diffraction analyses were performed on an ARL X'tra diffractometer (Thermo-Scientific). Flame Atomic Emission spectroscopy (AES) was performed on a Varian...
SpectrAA 220FS, using 4 bar acetylene and 0.7 bar nitrous oxide. Adsorption tests were performed using a thermostatatic shaking device (Infors HT Multitron standard, Analis, 25 °C, 220 rpm, 24 hours). In a typical adsorption test, 50 mg of adsorbent was added to 50 ml of aqueous 100 ppm Eu³⁺-solution (pH 4 with HCl) in glass vials (w/ plastic lids). The tests were performed in triplicate. The europium concentration before and after the tests was analysed by means of Flame-AES.

**Results and Discussion**

**Build-up of the CMPO-ligand onto the MIL-101**

Figure 3 gives an overview of the functionalization process of the MIL-101(Cr). In the first step, the material was chloromethylated to provide a proper anchoring point for further functionalization. In this procedure the sample (1 g) was suspended in 70 mL of nitromethane. Subsequently 1.9 g of AlCl₃·6H₂O and 0.4 g of methoxyacetyl chloride were added. The mixture was then stirred for 5 hours at 100 °C, after which the solid material was filtered off and washed thoroughly with nitromethane, water and acetone. The sample was then vacuum dried at 120 °C for 24 hours. The material was analysed for its chlorine content prior and post chloromethylation with XRF and was found to contain ~5 mmol chloromethyl-groups per gram material. The chloromethylated MOF (1 g) was then reacted with 1,4-diaminobutane (2.2 g) in 70 mL of DMF under inert atmosphere, by letting the mixture stir for 24 hours at 80 °C (Step 2). The material was filtered off, thoroughly washed with DMF and acetone, and vacuum dried at 120°C prior to elemental analysis. The sample contained approx. 5.5 wt.% additional nitrogen after this functionalization step, corresponding to 2 mmol dianiminobutane per gram. Current research is focussing on increasing this loading. The third step involves the coupling of the carboxylic end-groups of diethylphosphonoacetic acid with the primary amines of the functionalised MOF, forming the amide part of the CMPO-ligand. A total of 500 mg of amine-functionalised MOF is suspended in 25 mL of anhydrous DMF. In a separate round-bottom flask, 0.6 g of diethylphosphonoacetic acid (3 mmol) is dissolved in anhydrous DMF at room temperature (inert atmosphere), after which an equimolar amount of carbonyldiimidazole (CDI, 0.48 g) is added and the mixture is moderately stirred.¹⁰
Figure 3: Stepwise build-up of the CMPO-ligand on MIL-101(Cr). Initial MOF: MIL-101, chloromethylated: -Cl, aminated: -NH2, full ligand on MOF: MIL-101-LIG.

CDI is a known coupling agent for peptide synthesis, requiring water-free conditions\textsuperscript{14}. The reaction of CDI with the carboxylic end-group can be visually monitored because the mechanism leads to formation of CO\textsubscript{2}. The mixture is stirred until the evolution of CO\textsubscript{2} ceases (about 15 minutes). Afterwards both mixtures are combined and stirred for another 12 hours at room temperature. After filtration and washing with DMF, water, and acetone the sample is vacuum dried at 120 °C.

The following characterization analyses were performed on each stage of the (un)functionalised material: (1)nitrogen sorption measurements to determine the specific surface area of the material, which indicates the anchoring of species (weight-based result) and indirectly confirms the (in)stability of the material in the respective reaction conditions (shape of the isotherm); (2)DRIFTS-analyses to confirm whether the proper groups are anchored onto the material; (3)XRF-measurements to estimate the loading of the final ligand (via phosphorous analysis); (4) XRD measurements to further confirm the stability of the material in each step. The results are depicted in figures 4 to 6.
Figure 4: Nitrogen adsorption isotherm of the unfunctionalised MIL-101 (●), aminated MIL-101 (---) and finalised ligand MIL-101 (—).

Figure 5: DRIFTS spectra of each step in the functionalization. Inset: zoom on the aliphatic stretch region.
Figure 6: Powder XRD patterns of the (un)functionalised materials.

From the preservation of the XRD pattern and shape of nitrogen adsorption isotherm, it can be concluded that the MIL-101 perfectly maintains its structure throughout the different functionalization steps. Starting out at $S_{\text{Langmuir}}$: 3000 m$^2$/g, the MIL-101 gradually decreases in specific surface area upon each functionalization step due to anchored species that fill up the cages and increase the weight of the material. In the DRIFTS spectra aliphatic CH stretches appear (2850 – 3000 cm$^{-1}$, inset), confirming the presence of diaminobutane in the aminated sample and the final adsorbent. An indication of amine groups is visible near 1550 and 1650 cm$^{-1}$, corresponding to primary-NH$_2$ scissoring. These do not appear as isolated peaks but partially overlap with vibrations originating from the MIL-101 structure. In the spectrum of the finalised adsorbent, vibrations are visible at 1040 cm$^{-1}$ and in the region between 1200 and 1260 cm$^{-1}$. These indicate the P-OR ester and the phosphine oxides or phosphonates vibrations, respectively. Presence of other characteristic peaks could not be proven unambiguously due to overlap with the MIL-101 structural vibrations and possible low loading.

XRF-analyses showed a phosphorous-loading of 0.7 mmol/g, which indicates that not all primary amines have been functionalised with the phosphonoacetic acid group. Current research focusses on increasing the yield of this solid-phase peptidization.

The CMPO functionalised MIL-101 was tested in the adsorption of europium. The unfunctionalised MOF as well as the aminated one were tested in the same conditions and were found to be inactive for the adsorption of Eu$^{3+}$. The results of the final adsorbent are presented in table 1.

Table 1: Adsorption capacity of the CMPO functionalized MOF.

<table>
<thead>
<tr>
<th>Material</th>
<th>Functional group</th>
<th>$q_e$ (mg/g)</th>
<th>$q_a$ (mmol Eu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-101-Full Ligand</td>
<td>-CMPO</td>
<td>17 (±2)</td>
<td>0.11 (±0.01)</td>
</tr>
</tbody>
</table>

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The amount of europium adsorbed is calculated using the following expression:

\[ q_e = \frac{C_0 - C_e}{m} \cdot V \]

where \( q_e \) is the equilibrium adsorption capacity of europium (mg/g), \( C_0 \) and \( C_e \) the initial and equilibrium Eu\(^{3+}\) concentration (mg/L) respectively, \( V \) the solution volume (mL) and \( m \) the adsorbent mass (mg). A total of 17 mg Eu\(^{3+}\)/g (0.11 mmol/g) is adsorbed with 0.7 mmol/g of CMPO ligands. This corresponds to six or seven ligands for every Eu\(^{3+}\). The exact manner of coordination or the number of ligands coordinating to one europium is not yet determined.

**Conclusion**

The MIL-101(Cr) is successfully functionalised and applied for the first time as a rare earth metal adsorbent in acidic aqueous solution. The solid is post-modified via three subsequent steps which resulted in a material with 0.70 mmol per gram of carboxamoylmethylphosphine oxide ligands. The CMPO-functionalised MOF was used in preliminary experiments as a europium adsorbent and was able to adsorb \( \sim \)17 mg Eu\(^{3+}\)/g. More in-depth europium adsorption experiments will be performed including regeneration of the CMPO functionalised MOF adsorbent.

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MAGNETIC METAL OXIDE BASED ADSORBENT FOR EXTRACTION AND SEPARATION OF REE

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Abstract

Mesoporous transition metal oxides with high surface area (over 200 m\textsuperscript{2}/g) can efficiently be produced by a thermohydrolysis approach from solid metal alkoxides precursors. There materials can be made magnetic via insertion of iron oxide nanoparticles. Protection of materials against acid leaching is achieved by deposition of a thin layer of TiO\textsubscript{2}. The produced materials are easily modified by grafting of phosphonate ligands leading to creation of hybrid adsorbents conserving the morphology and surface characteristics of the applied oxide matrices. Aminopropyl phosphonic and imino(dimethylphosphonic) acids were used to achieve a proof-of-concept. The obtained adsorbents revealed good adsorption capacity towards REE cations (0.18, 0.21, 0.23 and 0.24 mmol/g for Y, Nd, La and Dy respectively). The obtained materials can be used for water purification and for recycling of REE.

Introduction

Mesoporous transition metal oxides constitute an attractive class of materials due to a broad spectrum of applications, ranging from heterogeneous catalysts \cite{1}, as matrices for catalyst deposition \cite{2}, electrode materials for metal ion batteries \cite{3}, dye-sensitized solar cells \cite{4}, and functional adsorbents for removal of radioactive \cite{5} and heavy metal pollutants \cite{6} from ground and waste waters. To be attractive for all these potential uses, the metal oxides should possess a high active surface area, considerable chemical stability to different types of leaching and dissolution, and in many cases be essentially pure from residual organics that may deteriorate the surface characteristics required for alkali metal ion insertion and heavy metal adsorption. Most often such materials are produced using either large organic or macromolecular templates \cite{7} and therefore need to undergo long term solvothermal treatment to improve their crystallinity. Alternatively, these materials can be synthesized in the absence of a template under rather extreme solvothermal conditions but still require calcination for removal of the organic residues \cite{8}.
Sol-gel synthesis using metal alkoxides as precursors is potentially a very promising route for production of mesoporous oxides. Depending on the nature of the alkoxide groups and introduced hetero ligands, it is possible to influence the size of the particles and their crystallinity [9]. The latter is improved by use of increased temperature and with more efficient removal of the ligands. Thus highly crystalline single nanoparticles of titania have been produced by immersion of solid titanium alkoxide modified with highly hydrophilic amino acid ligands into boiling water [10]. In a recent study we have shown that by using solid metal alkoxides derived from highly volatile alcohols (i.e. MeOH and EtOH), with reaction in boiling water, it is possible to produce materials with high crystallinity and open mesoporosity, thereby exploiting the evaporation of ligands as a tool to prevent collapse of the pores [11, 12].

A large surface charge with a dominating total negative charge in a broad pH interval [13], together with enhanced chemical affinity to highly charged anions makes these materials efficient as adsorbents in immobilization of a broad spectrum of solute species. The adsorbates include heavy metal cations such as uranium and thorium [14], various toxic anions, for example, arsenate [AsO$_4^{3-}$] [15] and phosphate or phosphonate [16] anchoring moieties. The adsorption processes rely on the molecular details of the interactions on the surfaces, and nanomaterials with their very large surface-to-volume ratio are especially attractive adsorbents. In the case of TiO$_2$, very large surface-to-volume ratios are available in the form of nanotubes or nanorods that can be produced in high yields by acidification and subsequent exfoliation of layered alkali metal titanates [17] or simply by electrospinning [18]. An interesting alternative for a facile and cost-efficient production of porous titania (anatase) nanorods is the so-called rapid hydrothermal synthesis. It makes use of nanorods of a metal-organic precursor titanium methoxide, Ti(OCH$_3$)$_4$ as a starting material [11]. The inexpensive and efficient surfactant-free synthesis of nano titania make related materials attractive alternatives to mesoporous silica adsorbents.

Titania-based adsorbents can be surface modified for potential uses in various applications. Its surfaces can be modified by carboxylates, phosphates and phosphonates moieties carrying a wide range of organic functionalities. In addition, such modifications allow TiO$_2$ nanoparticles to be stabilized in both aqueous [18] and hydrocarbon [19] media. They have also been converted into hybrid organic-inorganic materials with principally changed hydrophilicity/hydrophobicity and functionality, applied, for example, in the sorption of CO$_2$ from gas mixtures [20, 21], in separation of hydrophobic dyes from diluted solutions [22] and in extraction of heavy metal cations [23]. Among those a special attention has recently been focused on Rare Earth Elements (REE). REE, and especially neodymium (Nd) and dysprosium (Dy) are required for production of magnetic materials used both in electronics [24] and novel energy production technologies utilizing renewable energy sources [25], and are available as components in ores abundant in the Northern Europe, Iceland, Greenland, USA and Canada. Their production today is, however, almost exclusively concentrated to China,
where they are present in more easily exploitable forms and where the environmental hazards associated with their extraction and separation (in the first hand, production of huge volumes of acidic wastes and the use of huge volumes of organic solvents) are not treated with the same care. Also, the adsorption of actinide elements accumulating in the nuclear waste and displaying solution behavior analogous to REE became a topic of increased attention in connection with recent disaster at the Fukushima nuclear plant [26]. An effort has been reported recently in creation of hybrid mesoporous silica based adsorbents bearing alkyl phosphonate function for selective adsorption of REE [27].

In the present work we discuss results from studies of hybrid adsorbents produced from mesoporous metal oxides, in the first hand, titania nanorods. They were derived by a precursor-driven approach [11] via straightforward immobilization of aminoethylphosphonic acid AEPA (NH$_2$(CH$_2$)$_2$PO$_3$H$_2$) and imino-bisphosphonic acid IMPA (NH(CH$_2$PO$_3$H$_2$)$_2$) on the surface of nanoparticles. As shown, this approach permits a denser grafting on the titania surface than other approaches [16], and thus these sorbents have a potentially much higher adsorption capacity.

**Results and Discussion**

Synthesis of the oxide material was carried out using a unified procedure by rapid immersion of the precursor powder into boiling water with subsequent refluxing for 30 min. All oxide materials produced are mesoporous and demonstrate nitrogen sorption isotherms of type IV according to IUPAC classification (see Fig. 1).

![Figure 1. Nitrogen sorption isotherms for mesoporous oxides obtained by thermohydrolytic treatment of Ti(OMe)$_4$ (a), Zr(OPr)$_4$(iPrOH) (b), Nb(OMe)$_5$ (c), Zr(OEt)$_4$ (d) and Ta(OMe)$_5$ (e). They possess impressively high active surface areas and pore volume fractions (see Tab. 1) with a sharp pore size distribution and well defined maximum in the meso scale.](image-url)
Table 1: Textural characteristics of metal oxides produced by thermohydrolysis

<table>
<thead>
<tr>
<th>Metal oxide $^{[a]}$</th>
<th>Precursor</th>
<th>Active surface area, m²/g$^{[b]}$</th>
<th>Mean pore size, nm$^{[c]}$</th>
<th>Pore volume, cm³/g$^{[d]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>Ti(OMe)₄</td>
<td>278</td>
<td>5.1</td>
<td>0.43</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Zr(OEt)₄</td>
<td>257</td>
<td>3.2</td>
<td>0.20</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Zr(O₂Pr)₄(iPrOH)</td>
<td>321</td>
<td>5.1</td>
<td>0.41</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>Nb(OMe)₅</td>
<td>410</td>
<td>2.9</td>
<td>0.29</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>Ta(OMe)₅</td>
<td>98</td>
<td>3.8</td>
<td>0.09</td>
</tr>
</tbody>
</table>

$^{[a]}$ Data after initial drying at 120°C for 3h. $^{[b]}$ Calculated using BET method. $^{[c]}$ and $^{[d]}$ calculated using BJH method on the desorption branch and at p/p₀=0.99 respectively

Magnetic properties were introduced via insertion of magnetite nanoparticles. The Fe₃O₄ was obtained in nano form by co-precipitation and used in aqueous dispersion as solution for thermohydrolysis of the alkoxides precursors. The freshly produced material was covered by thin layer of TiO₂ using CaptiGel™ aqueous titania to insure stability in acidic media. The produced material displayed strong magnetic properties (Fig. 2).

![Figure 2. Magnetization versus field at T=10K (uncoloured) and T = 300 K (coloured) for titania-iron oxide adsorbent](image)

Grafting of functional phosphonate ligands was achieved at room temperature by stirring the matrices in a ligand solution in 48 h. The ceramic yields for the adsorbents were for both ligands ~ 70%, and the inorganic-organic hybrid materials were separated by straightforward sedimentation overnight. The deviation from a quantitative yield was ascribed to a partial stabilization in solution of small and non-precipitating nanoparticle aggregates, splitting from the body of nanorods on mechanical treatment (stirring in 72 h), by the adsorbed amino phosphonic ligands.
The adsorption of amino phosphonate ligands has already been reported to stabilize dispersions of small non-aggregated metal oxide nanoparticles [16]. The effect was more pronounced for AEPA than for IMPA, as it has been observed previously for other oxide systems [16].

An insight into surface coordination of the amino phosphonic acids onto TiO₂ is provided by their FTIR spectra. As reported in literature [28], AEPA can form molecular zwitter-ionic structure in the spectrum of which the vibrational bands relating as to the bending NH₃⁺ modes of the initial acid are located at 1482 cm⁻¹ [δₛNH₃] and 1643 cm⁻¹ [δₐsNH₃]. During modification of the surface of titanium dioxide by AEPA the phosphonate groups are involved into complex formation and possibly deprotonation, leading for the TiO₂-AEPA sample to the shift of the δₛNH₃ adsorption band to 1510 cm⁻¹. The FTIR spectra demonstrate thus that the ligands are definitely located on the surface after grafting and that at least AEPA is present there in zwitter-ionic form, indicating possibility that this acid can be connected to the TiO₂ surface with release of only one proton.

Sorption kinetics of Dy³⁺ cations from aqueous solutions were investigated for both TiO₂-AEPA and TiO₂-IMPA (see Fig. 3)

![Figure 3. Kinetics of Dy³⁺ ions sorption by samples TiO₂-IMPA and TiO₂-AEPA](image)

The dynamic equilibrium in REE adsorption was achieved for both TiO₂-AEPA and TiO₂-IMPA within 72 h. Such considerable delay in reaching the equilibrium is usually a feature of mass transport limitations within the materials. These limitations appear logical due to the ink-bottle shaped pores that were indicated in the N₂ desorption characteristics in these adsorbents. The Dy³⁺ adsorption by TiO₂-IMPA was faster than on TiO₂-AEPA, and was completed to 95% within 24 h.

The sorption isotherms obtained for Y³⁺, La³⁺, Nd³⁺ and Dy³⁺ cations (see Fig. 4) belong to the Langmuir type indicating similar sorption mechanisms in all cases. All isotherms had slight kinks in the equilibrium concentration region of 0.05-0.2 mmol/l. These kinks could speculatively indicate potential conformational changes for the ligands in the surface layer on TiO₂.
Figure 4. Sorption isotherms of Nd$^{3+}$ and Dy$^{3+}$ on TiO$_2$, functionalized with aminophosphonic acids.

The obtained adsorbents show thus relatively modest values of static sorption capacity (SSC) and compared with the best silica-based mesoporous nanoabsorbents constituting the state-of-the-art in the field [29, 30]. However, our results are impressively better than those from analogous experiments with hybrid organic-inorganic adsorbents based on ZrTi-0.33 mesoporous adsorbent functionalized with, in particular, amino tris(methylphosphonic) acid: the TiO$_2$-AEPA shows about 10 times and TiO$_2$-IMPA up to 50 times higher adsorption capacity [27]. Much lower price of mesoporous titania prepared by the utilized approach makes the produced material potentially interesting for remediation applications. The better efficiency in ligand involvement in adsorption revealed by the TiO$_2$-IMPA material provides it with 3-4 times higher capacity compared with TiO$_2$-AEPA.

**Conclusions**

A simple and efficient methodology for preparation of hybrid magnetic adsorbents based through grafting of amino phosphonate ligands on the surface of mesoporous titanium dioxide was developed. The ligand loading varies for different ligands in the range 0.17-0.21 mmol/g. The pore volume and active surface area undergo minor decrease as a result of this transformation. By comparing the data from several experimental methods it appeared as the ligands are bound to the TiO$_2$ surface through loss of one proton per ligand. The adsorption of REE, Y$^{3+}$, La$^{3+}$, Nd$^{3+}$ and Dy$^{3+}$, cations from weakly acidic solutions was associated with a considerable decrease in the pH, which indicating an ion exchange mechanism for this process. The uptake of REE varied in the range 0.18-0.24 mmol/g corresponding to M:L = 1:1 surface complexes being formed. This value is comparable with capacity of organic ion-exchange resins. The produced adsorbents are of interest in separation of REE for water purification and for recycling processes.
References


ORGANIC-LIGAND GRAFTED MAGNETIC NANOADSORBENTS FOR EXTRACTION AND SEPARATION OF REE.

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Abstract

Magnetic hybrid nanoadsorbents functionalized with different organosilane derivates were synthesized and their affinity to Rare Earth Elements (REE) cations in solution was tested. Magnetite Fe₃O₄ nanoparticles (MNP) were chosen as cores because of their good magnetic properties and stability. The MNP were synthesized and coated with SiO₂ resulting in highly stable core-shell Fe₃O₄@SiO₂ nanoparticles. Three different organic chelators were synthesized and attached to the surface of core-shell structures and to the surface of SiO₂ nanoparticles, which were used as prototypes. Ligand grafting was assed by FTIR, TGA and ¹H and ²⁹Si Solid State NMR. Dy³⁺ and Nd³⁺ uptake capacity was tested in both static and dynamic conditions and studied by SEM-EDS and complexometric titrations respectively.

Scheme 1. Design of the magnetic nanosorbent materials
Introduction

Lanthanide based materials have gained a lot of importance due to their wide range of applications, such as high field strength magnets\(^1\), sensors\(^2\), electrooptical devices\(^3\), catalysts\(^4\) etc. This increasing demand for lanthanides resulted in an increased production of lanthanide through mining. Therefore, separation and purification of lanthanides from ores urges development and optimization of new technologies. Among them, one can find high affinity sorbents for sequestration of the lanthanides from diluted industrial waste streams or the removal/sorption and extraction from mine leachates. Furthermore, sorbent materials should be economical and reusable in order to be feasible for industrial application as well as environmentally friendly in order to reduce the environmental burden after use\(^5\).

For this reasons, a special interest was set to magnetic iron oxide nanoparticles for facilitated removal of adsorbed content. Iron oxide nanoparticles have many advantages due to their high magnetism and good stability as well as less toxicity when compared with their metal magnetic counterparts like iron and cobalt\(^6\), which is very important specially for environmental applications. Despite their good stability, it is necessary to coat their surface with an organic or inorganic shell in order to protect them from chemical degradation or agglomeration\(^7\). Among different types of coating materials, silica coating is one of the most advantageous methods due to its stability in aqueous solution. Silica coating allows protection of the magnetic cores and prevents the direct contact of the magnetic core with external agents or structures linked to the surface, enhances their biocompatibility, hydrophilicity and dielectric properties\(^8\). Furthermore, it also facilitates surface modification due to the silanol groups (-SiOH) on the surface of silica\(^9\).

Heavy metal adsorption and ligand conjugated magnetic separation have been extensively studied in water treatment and environmental cleanup\(^10\), but there are not so many studies regarding the removal of rare earth ions (RE\(^{3+}\)) from industrial waste water or mining leachates with iron oxide nanoparticles. Binnemans and co-workers\(^11\) have studied uptake capacity of all lanthanides serie (La\(^{3+}\), Pr\(^{3+}\), Nd\(^{3+}\), Sm\(^{3+}\), Gd\(^{3+}\), Tb\(^{3+}\), Dy\(^{3+}\), Ho\(^{3+}\), Er\(^{3+}\), Yb\(^{3+}\), Lu\(^{3+}\)) in aqueous solution using EDTA functionalized magnetic (Fe\(_3\)O\(_4\)) and non-magnetic (SiO\(_2\) and TiO\(_2\)) nanoparticles.

In the present work, highly stable core-shell Fe\(_3\)O\(_4@\)SiO\(_2\) nanoparticles were synthesized and surface modified with organic chelates. Pure SiO\(_2\) nanoparticles were also surface modified with the same organic ligands and used as prototypes. Adsorption behaviour of all the materials towards Dy\(^{3+}\), Nd\(^{3+}\) and La\(^{3+}\) was tested by SEM-EDS, complexometric titrations and luminescent measurementes in the case of silica prototypes. Selectivity with Nd/Dy and La/Dy binary rare earth mixtures was also investigated by SEM-EDS.
Results and Discussion

Optimization and effects of reaction parameters for Fe₃O₄ nanoparticles and core-shell Fe₃O₄@SiO₂ nanoparticles

The most simple and efficient method for synthesis of Fe₃O₄ nanoparticles is the coprecipitation of iron salts¹²,¹³, which is performed under non-oxidizing environment using a stoichiometric ratio of 2:1 Fe³⁺/Fe²⁺ in aqueous solution followed by the addition of NH₄OH solution.

The as-synthesized Fe₃O₄ nanoparticles were succesfully coated by silica using Stöber method¹⁴, which is based on the alkaline hydrolisis of tetraethyl ortosilicate (TEOS). Two different synthetic procedures were carried out (reaction parameters are shown in Table 1) leading to nanoparticles with different size and physical properties.

Table I. Reaction parameters for Fe₃O₄@SiO₂ nanoparticles synthesis

<table>
<thead>
<tr>
<th>No</th>
<th>Fe₃O₄ (mmol)</th>
<th>H₂O (mL)</th>
<th>Ethanol (mL)</th>
<th>NH₄OH (mmol)</th>
<th>TEOS (mmol)</th>
<th>Hours (h.)</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.4</td>
<td>-</td>
<td>40</td>
<td>270</td>
<td>11.8</td>
<td>2</td>
<td>800</td>
</tr>
<tr>
<td>II</td>
<td>0.4</td>
<td>32 mL</td>
<td>160</td>
<td>53.4</td>
<td>7.0</td>
<td>20</td>
<td>100</td>
</tr>
</tbody>
</table>

For our purpose, it is very important to achieve small particles since they lead to materials with higher surface area allowing the binding of higher amounts of organic ligands, which facilitates the coordination with rare earths in solution. Therefore, the second synthetic pathway, previously reported on the literature⁷b,¹⁵, is more suitable since it leads to nanoparticles with an average diameter of 100 nm (±15nm) according to TEM results, which also confirms the effectiveness of Stöber method for silica coating showing a silica shell of approximately 25 nm. (Figure 1).
For industrial purposes, it is very important that the core-shell nanoparticles are stable under acidic conditions in order to resist the process of separation from ores or aqueous solution. Stability for these particles was tested with a solution of HNO₃ 0.1M containing KSCN 0.5%.

The Fe₃O₄@SiO₂ nanoparticles synthesized under synthetic pathway II are very stable under time. Even after 5 months, there was no sign of iron leaching in the solution. In order to be able to compare, images from nanoparticles synthesized according synthetic pathway I are also shown (Figure 2), with a molar ratio TEOS/Fe₃O₄ of 0.125, in which iron did leach from the solution.

**Adsorption of lanthanides (Dy³⁺ and Nd³⁺) on ligand grafted SiO₂ nanoparticles**

Determination of lanthanides uptake of the produced ligand grafted nanoparticles was carried out by complexometric titration given the known concentration of initial lanthanides in solution which is put in contact with the sorbent materials. EDTA complexates metals in a 1:1 ratio, therefore a complexometric titration can be carried out with the remaining solution after sorption, and the amount of lanthanides uptaken can be calculated by subtractions, since the initial amount is known and the remaining amount is determined. To 50 mg of organic ligand grafted SiO₂ nanoparticles (L2 and L3 were tested), a calculated amount of lanthanide salt solutions (equivalent to the moles of ligand grafted on the surface, calculated from TGA analysis) was added. NaNO₃ was added to facilitate sorption and the mixtures were stayed in static
conditions for different times (2, 8, 24 and 48 hours). After that time the samples were centrifuged and washed one time and the remaining solutions were titrated with EDTA.

Kinetic curves obtained by these reverse complexometric titrations show a quick achievement of the lanthanides adsorption equilibria (Figure 2). A higher affinity to Nd3+ ions can be observed for Ligand-2 grafted SiO2 nanoparticles whereas ligand-3 grafted SiO2 nanoparticles have higher affinity to Dy3+ ions. Uptake capacity is, in the case of ligand-3 grafted SiO2 nanoparticles, very reasonable for static sorption processes, resulting in an efficient material comparable to ion exchange resins16,17 (Table 2).

Figure 2. Kinetic curves of Dy3+ and Nd3+ static sorption process on hybrid silica nanoparticles

Table 2. Lanthanides uptake capacity of hybrid silica nanoparticles in static sorption conditions

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Dy3+ adsorbed (mmol Dy3+/g sample)</th>
<th>Nd3+ adsorbed (mmol Nd3+/g sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO2@L2</td>
<td>SiO2@L3</td>
</tr>
<tr>
<td>2</td>
<td>0,013</td>
<td>0,186</td>
</tr>
<tr>
<td>8</td>
<td>0,029</td>
<td>0,187</td>
</tr>
<tr>
<td>24</td>
<td>0,029</td>
<td>0,198</td>
</tr>
<tr>
<td>48</td>
<td>0,043</td>
<td>0,233</td>
</tr>
</tbody>
</table>
Adsorption of lanthanides (Dy$^{3+}$, Nd$^{3+}$ and La$^{3+}$) on surface modified iron oxide nanoparticles

Same complexometric determination with Na$_4$EDTA was carried out for ligand grafted iron oxide nanoparticles. Ligand 3 was used in this study because it showed to be the most suitable for adsorption.

Kinetic curves show a quick achievement of the lanthanides adsorption equilibria (Figure 3), reaching in the three cases more than 65% of the maximum uptake in 2 hours. Uptake capacity is, for the three lanthanide ions very reasonable and effective for static sorption processes, resulting in an efficient material for adsorption (Table 3). The best uptake capacity was achieved for Dy$^{3+}$, with a maximum uptake of 0.25 mmol/g (equivalent to 40 mg Dy$^{3+}$/g), whereas maximum uptake was 0.23 mmol/g for Nd$^{3+}$ (equivalent to 33.6 mg Nd$^{3+}$/g) and 0.2 mmol/g for La$^{3+}$ (equivalent to 27.8 mg La$^{3+}$/g).

Table 3. Lanthanides uptake capacity of modified iron oxide nanoparticles in static sorption conditions

<table>
<thead>
<tr>
<th>Time</th>
<th>Dy$^{3+}$ ads. (mmol Dy$^{3+}$/g)</th>
<th>Nd$^{3+}$ ads. (mmol Nd$^{3+}$/g)</th>
<th>La$^{3+}$ ads (mmol La$^{3+}$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.17</td>
<td>0.21</td>
<td>0.18</td>
</tr>
<tr>
<td>8</td>
<td>0.18</td>
<td>0.20</td>
<td>0.14</td>
</tr>
<tr>
<td>24</td>
<td>0.23</td>
<td>0.23</td>
<td>0.19</td>
</tr>
<tr>
<td>48</td>
<td>0.25</td>
<td>0.23</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Lanthanides selectivity studies on ligand grafted SiO₂ nanoparticles and surface modified iron oxide nanoparticles

Selectivity on binary rare-earth mixtures was tested on the ligand grafted SiO₂ nanoparticles and the surface modified iron oxide nanoparticles. Nd/Dy and La/Dy mixtures were used in a 1:1 molar ratio of lanthanide: ligand. Total uptake was determined by complexometric titrations carried out as previously explained and lanthanides selectivity was studied by SEM-EDS analysis.

Tables 5-6 show the total uptake capacity and SEM-EDS surface characterization for all the materials tested. It is necessary to remark that EDS analysis is very influenced by the heterogeneity and roughness of the surface sample, but it is helpful to give a qualitative estimation of the selectivity, showing a quite clear selectivity towards Dy³⁺.

Table 5. Lanthanides mixtures total uptake capacity of different materials in dynamic sorption conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lanthanides</th>
<th>Uptake capacity (mmol Ln³⁺/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄@SiO₂@L₃</td>
<td>Nd-Dy</td>
<td>0.127</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂@L₃</td>
<td>La-Dy</td>
<td>0.026</td>
</tr>
<tr>
<td>SiO₂@L₃</td>
<td>Nd-Dy</td>
<td>0.242</td>
</tr>
<tr>
<td>SiO₂@L₃</td>
<td>La-Dy</td>
<td>0.275</td>
</tr>
</tbody>
</table>

Figure 3. Kinetic curves of Dy³⁺, Nd³⁺ and La³⁺ static sorption process on modified iron oxide nanoparticles
Table 6. EDS analysis of sorbent materials with binary rare earths mixtures

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Nd molar</th>
<th>%La molar</th>
<th>%Dy molar</th>
<th>Dy/Nd molar ratio</th>
<th>Dy/La molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄@SiO₂@L3 Nd-Dy neutral pH</td>
<td>1,017061</td>
<td>-</td>
<td>0,763981</td>
<td>0,751166</td>
<td>-</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂@L3 La-Dy neutral pH</td>
<td>-</td>
<td>0,214887</td>
<td>0,439505</td>
<td>-</td>
<td>2,045283</td>
</tr>
<tr>
<td>SiO₂@L3 Nd-Dy neutral pH</td>
<td>0,96066</td>
<td>2,362555</td>
<td>2,459304</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂@L3 La-Dy neutral pH</td>
<td>-</td>
<td>1,164047</td>
<td>3,49001</td>
<td>-</td>
<td>2,998169</td>
</tr>
</tbody>
</table>

Conclusions

New magnetic nanosorbents with high stability under acidic conditions (over 5 months) were produced and their lanthanides uptake capacity was tested in neutral pH conditions, showing in many cases capacities comparable with ion exchange resins. Selectivity with binary rare earths mixtures was also tested and showed effective selectivity towards Dy³⁺.

References


APPLYING IONIC LIQUIDS TO RARE-EARTH SEPARATIONS

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Abstract

A way to improve the sustainability of solvent extraction is to replace the organic diluents used in current separation processes by ionic liquids. The desirable properties of ionic liquids include a very low vapour pressure, which avoids air pollution and reduces the risk of fire. In order to successfully apply ionic liquid systems to rare-earth separation processes these systems need to be economic, simple and give high separation factors. For this purpose, undiluted ionic liquids with quaternary ammonium and phosphonium cations with nitrate anions have been investigated for the extraction of rare earths from aqueous nitrate solutions using EDTA as an aqueous complexant. At higher rare-earth concentration levels, the distribution ratios are loading-dependent making the extraction dependent on the composition of rare earths. Therefore the composition was modelled on the European deposit of Norra Kärr (Sweden).

Introduction

The use of ionic liquids for the separation of mixtures of rare earths through solvent extraction is a developing field with high potential because of both the intrinsically beneficial properties of ionic liquids and the suitable extraction properties of some ionic liquids.1-3 Ionic liquids are per definition solvents consisting solely of ions and are typically made up of salts with organic components and are liquid at useful temperatures. The properties of ionic liquids generally include a very low vapour pressure. This can make incorporating them into solvent extraction processes a part of the transition towards greener processes since this reduces flammability and air pollution.1 Ionic liquids can however only be considered green provided that they have a low persistency and a low toxicity. A part of this is the avoiding the use of fluorinated ionic liquids, due to their persistence in nature.4

Two reasonable starting points when using undiluted hydrophobic ionic liquids, without functional groups specific to rare-earth extraction, are choosing a suitable counter-ion that will create extractable complexes with the rare earths to be extracted and choosing an ionic liquid with properties suitable for solvent extraction. For the counter-ions, the most obvious choices are sulphate, chloride or nitrate, since the corresponding acids (H2SO4, HNO3, HCl) can be used to dissolve rare-earth-containing...
starting materials. Sulphuric acid is somewhat unsuitable due to the low solubility of some rare-earth sulphate salts in solutions with high sulphate concentrations. Hydrochloric acid is a potential choice since rare-earth chloride complexes can be extracted using chloride ionic liquids, though only at very high chloride concentrations, although suitable solvating extractant extractants can be used to extract from chloride systems.6–8 The chloride-chloride (chloride in both phases) ionic liquid systems, such as tricaprylmethylammonium chloride for extraction of rare earths from chloride aqueous solutions, are unsuitable due to low distribution ratios.

Nitrates have historically been used for rare-earth separation systems since nitrates form highly extractable complexes with rare-earth ions. The use of tricaprylmethylammonium nitrate in rare-earth separation has strong precedents in the literature, with a number of investigations and patents, but these extractants are usually used diluted in molecular diluents and not as pure ionic liquids.9–17 Two commercially available non-fluorinated hydrophobic ionic liquids suitable for solvent extraction were therefore chosen for this study: tricaprylmethylammonium chloride (Aliquart 336) and trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101), both of which can have their chloride anions easily replaced by nitrate ions. These ionic liquids can also be used as diluents for other ionic liquids or classical extractants due to their physical properties, including a comparatively (to other ionic liquids) low viscosity when equilibrated with a water phase.

Gaudernack et al. described the use of quaternary ammonium nitrate dissolved in organic diluents to extract light rare earths from an aqueous nitrate solution, followed by extraction of the heavy rare earths using a quaternary ammonium thiocyanate dissolved in organic solvents for the primary purpose of separation yttrium from the other rare earths.16 This process has an optimum at a nitrate concentration in the range of 5–7 M, with 0.5 M or less of rare-earth metals, using a nitrate salt (e.g. sodium or ammonium nitrate). The given acidity is stated as a range of pH values between 0.5 and 5, where extractability is higher at higher pH and separation increased at lower pH. Modification of the separation factors by aqueous complexants such as diethylene triamine pentaacetic acid (DTPA), followed by stripping by ammonium chloride and subsequent precipitation by oxalic acid when using quaternary ammonium nitrates dissolved in organic diluents to selectively extract lighter lanthanides was described by Bauer et al.12. Trimble et al. described the use of an amine extractant to extract light lanthanide followed by an acidic extractant extraction to remove heavy lanthanides, with the purpose of attaining pure yttrium by stripping it using an acidic scrub.17 Morais et al. investigated the use of tricaprylmethylammonium nitrate dissolved in kerosene to separate gadolinium and europium in a sodium nitrate matrix with a separation factor of 2.0 that was independent of the nitrate concentration.10 Lu et al. investigated the separation of praseodymium from neodymium using 0.6 M
tricapryl methylammonium nitrate in an aromatic diluent with DTPA used as an aqueous complexant.\textsuperscript{11}

In this paper, we report on the separation of rare earths by extraction with tricapryl methylammonium nitrate or trihexyl(tetradecyl)phosphonium nitrate from an aqueous nitrate feed solution containing EDTA as complexant. The significant progress, compared to some previous studies, proposed in this work is to proceed towards greener processes for the separation of rare earths. This is achieved by use of nitrate ionic liquids in their pure form instead of diluted in, for example, kerosene in order to gain the benefit of ionic liquids and thereby having an insignificant vapour pressure. The fact that the concentration of the extractant is very high since the ionic liquid phase acts itself as the extractant also gives high distribution ratios. The growth in the number of products utilising rare-earth metals in their construction has led to a supply risk of rare earths which in turn has lead to the desire to develop geographically diverse resources of rare earths.\textsuperscript{18} This study therefore uses a European rare-earth source as a model for the distribution of the aqueous solutions used for extraction studies.

The aqueous complexing agent ethylenediaminetetraacetic acid (EDTA) was used to increase separation factors. EDTA was chosen because of its favourable properties since it forms more stable complexes with heavy rare earths than with light rare earths. This increases the separation factors, since the extractant is a quaternary ammonium or phosphonium salt that extracts light rare earths preferentially.

**Experimental**

Tricaprylmethylammonium chloride (Aliquat 336) is a mixed quaternary ammonium salt containing mainly triocymethylammonium and tridecylmethylammonium chloride (Sigma-Aldrich, 88.2-90.6%). Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) is a phosphonium-based ionic liquid (Cytec Industries, 97.7%). To prepare the nitrate form of the ionic liquids, they were pre-equilibrated three times for 1 hour or more with a 2.5 M KNO\textsubscript{3} solution to exchange the chloride ions by nitrate ions. After three equilibrations, the chloride levels in the ionic liquid phase were under the instrumental detection limits (TXRF).

Hydrated rare-earth nitrate salts were obtained from Aldrich (Y 99.9%, Tb 99.9%, Sm 99.9%), Alfa Aesar (La 99.99%, Nd 99.9%, Dy 99.9%, Ho 99.9%, Yb 99.9%), Chempur (Pr, 99.9%) and Acros (Gd 99.9%). The following rare earth oxides were used: yttrium(III) oxide (Rhodia, 99.99%), lanthanum(III) oxide (Aldrich, 99.99%), praseodymium(III,IV) oxide (Janssen chemicals, 99.9%), neodymium(III) oxide (Rhodia, 99.9%), samarium(III) oxide (Rare Earth Products Ltd, 99.9%), europium(III) oxide (InfraMat Advanced Materials, 99.99%), gadolinium(III) oxide (Ventron LFA
products, 99.9%), terbium(III,IV) oxide (Rare Earth Products Ltd, 99.99%), dysprosium(III) oxide (Rare Earth Products Ltd, 99.99%), holmium(III) oxide (Rare earth products Ltd, 99.99%), erbium(III) oxide (Acros Organics, 99.99%), thulium(III) oxide (GFS Chemicals, 99.9%), ytterbium(III) oxide (Rhodia, 99.9%), lutetium(III) oxide (Rare Earth Products Ltd, 99.9%). Ethylenediaminetetraacetic acid (Acros Organics, 99%) and potassium nitrate (Chem-lab, >99%). Sodium nitrate (Chem-Lab, >99%), ammonium nitrate (Chem-Lab, >99%). All dilutions were made using pure water (MilliQ, Millipore, >18 MΩ/cm). A Picofox S2 (Bruker) total reflection X-ray fluorescence (TXRF) spectrometer was used to determine the metal content in solutions.

Batch solvent extraction experiments were performed using approximately 1 mL of each phase, unless other phase ratios were tested, in which case the ionic liquid volume was increased. Samples were shaken at constant temperature (30 °C) using a TMS-200 turbo thermo shaker (Hangzhou Allsheng Instruments Co., Ltd) for 30 min, or longer when stated. The pH measurements were performed using a S220 SevenCompact pH/Ion meter (Mettler-Toledo) and a slimtrode electrode (Hamilton) and calibrated using pH 1.0 (Merck), 4.0 (Chem-Lab), 7.0 (VWR) and 10 (Fischer) buffers.

The distribution ratio (D) of a single metal is defined (equation 1) as the ratio of the total concentration in the ionic liquid phase ([M]_IL) by the total concentration in the aqueous phase ([M]_aq) after extraction and phase separation. The phase ratios are defined as the volume ionic liquid divided by the volume aqueous phase.

\[ D = \frac{[M]_IL}{[M]_aq} \]  

(1)

The basic assumption regarding the starting material was that an oxide concentrate has been formed from a starting ore material, thereby attaining an up-concentration and the possibility of choosing the chemistry of the separation process. The concentrate can in principle be in different forms such as oxide, carbonate, hydroxide, etc. The starting material for this work was based on a HREE-rich concentrates, such as the European deposit Norra Kärr in Sweden, with an average composition given in Table 1.19 This initial process development, described in this paper, did not include the common impurities of the deposits ore body (zirconium, manganese, iron, etc.). It is also assumed that cerium is removed by a separate process step prior to (or in combination with) the re-dissolution of the oxide material. The optimal conditions for the separation process are dependent on the starting material and on the chosen concentrations for the re-dissolution of the oxide material.

High concentration nitrate aqueous phases with and without EDTA were prepared by dissolving in nitric acid a mixture of rare-earth oxides with a composition distribution
mimicking that of the Norra Kärr deposit (Table 1, column A). A 6 M NaNO₃ matrix was spiked with a few representative rare-earth nitrate salts in order to study the nitrate extraction systems at low loading (Table 1, column B).

**Table 1:** Column A: composition of the concentrated rare-earth oxide solution in HNO₃. Column B: concentrations of the solution spiked with rare earths for low concentration, high matrix experiments (6 M NaNO₃).

<table>
<thead>
<tr>
<th>Metal</th>
<th>A (M)</th>
<th>B (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.23</td>
<td>0.011</td>
</tr>
<tr>
<td>Pr</td>
<td>0.08</td>
<td>0.012</td>
</tr>
<tr>
<td>Nd</td>
<td>0.23</td>
<td>0.012</td>
</tr>
<tr>
<td>Sm</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>0.068</td>
<td>0.0081</td>
</tr>
<tr>
<td>Tb</td>
<td>0.02</td>
<td>0.0054</td>
</tr>
<tr>
<td>Dy</td>
<td>0.084</td>
<td>0.0071</td>
</tr>
<tr>
<td>Ho</td>
<td>0.02</td>
<td>0.0096</td>
</tr>
<tr>
<td>Er</td>
<td>0.029</td>
<td></td>
</tr>
<tr>
<td>Tm</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>0.045</td>
<td>0.015</td>
</tr>
<tr>
<td>Lu</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>1.3</td>
<td>0.0095</td>
</tr>
</tbody>
</table>

**Results and Discussion**

**Extraction with nitrate-based ionic liquids**

The distribution ratios in Table 2 indicate that, if the nitrate concentration is sufficiently high, nitrate pre-equilibrated Cyphos IL 101 is suitable for extracting all rare earths together. Tricaprylmethylammonium nitrate is better suited for group separations than trihexyl(tetradecyl)phosphonium nitrate since the separation factors between light rare earths (e.g. La, Pr, Nd) and heavy rare earths (e.g. Yb) and yttrium is greater for tricaprylmethylammonium nitrate. There is also a significant difference in the mid-range elements (Gd, Tb, Dy, Ho) that could be exploited to separate these elements.
Table 2: Distribution ratios in tricaprylmethylammonium nitrate (A) and trihexyl(tetradecyl)phosphonium nitrate (B) using an aqueous phase of 6 M NaNO₃ spiked with rare-earth nitrate salts. 30 min of mixing at 30 °C.

<table>
<thead>
<tr>
<th>Metal</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>&gt;300</td>
<td>430 ± 140</td>
</tr>
<tr>
<td>Pr</td>
<td>&gt;250</td>
<td>230 ± 29</td>
</tr>
<tr>
<td>Nd</td>
<td>110 ± 13</td>
<td>200 ± 7.4</td>
</tr>
<tr>
<td>Gd</td>
<td>15 ± 1.0</td>
<td>74 ± 6.6</td>
</tr>
<tr>
<td>Tb</td>
<td>18 ± 1.2</td>
<td>120 ± 32</td>
</tr>
<tr>
<td>Dy</td>
<td>16 ± 1.6</td>
<td>86 ± 13</td>
</tr>
<tr>
<td>Ho</td>
<td>14 ± 1.5</td>
<td>72 ± 1.9</td>
</tr>
<tr>
<td>Yb</td>
<td>3.7 ± 0.7</td>
<td>18 ± 0.8</td>
</tr>
<tr>
<td>Y</td>
<td>4.7 ± 0.8</td>
<td>22 ± 1.1</td>
</tr>
</tbody>
</table>

However, the distribution ratios of ytterbium and yttrium are too high to be used for separations at the 6 M nitrate concentration. Therefore the distribution ratio was investigated as a function of the nitrate concentration between 3 M and 5 M nitrate by diluting the spiked 6 M sodium nitrate solution with pure water before contacting it with tricaprylmethylammonium nitrate (Figure 1). The separation factors remained constant over the range of nitrate concentrations while only the distribution ratios varied. The separation factors versus lanthanum for the heavy rare earths (Yb and Y) are approximately 200 while for the medium rare earths (Gd, Tb, Dy and Ho) the separation factors vary between 50 and 70.
Figure 1: Distribution ratios for tricaprylmethylammonium nitrate versus concentration of sodium nitrate (3–5 M) at 1 h of mixing, 30 °C, pH approximately 2.

The separation factors coupled with the relevant distribution ratios are sufficient for a process to separate the light rare earths from the heavy and medium ones. However, there will be significant co-extraction of both medium and heavy rare earths. To increase the separation factors, an additional component is needed. An aqueous phase complexant can be used to increase the separation factors and reduce co-extraction. A suitable aqueous complexant is EDTA, which has a varying complex strength across the lanthanide series with stronger complexes for the heavier rare earths. This interacts well with the nitrated ionic liquid system since the light rare earths are to be extracted and the heavy remain in the aqueous phase, which is strengthened by complexing with EDTA. Additionally DTPA, citric acid, lactic acid and malonic acid were investigated, but were found to have undesirable properties at high loading, primarily precipitation or too low solubility of the acid.

A more acidic medium was tested as well (6 M nitric acid), but only very poor rare-earth extraction was observed (D < 0.1). Acidic and non-acidified chloride systems were investigated in Cyphos IL 101 and Aliquat 336, using 4 M sodium chloride and 8 M hydrochloric acid; however, only poor (D < 0.1) or no extraction at all was observed.

Aqueous complexant assisted separation with tricaprylmethylammonium nitrate
To evaluate the influence of pH on a system with the aqueous complexant EDTA, the pH of a highly loaded system with a high EDTA concentration was varied between 1.5 and 3.75 (Figure 2). The distribution ratios were lower at low pH. This shows that the pH has an impact on the distribution ratios; however, the separation factors remain fairly constant, as shown in Figure 3. This means that the following investigations into the effect of lanthanide metal loading and EDTA concentration should have the same pH but that small variations will have only a small effect on separation factors.
Figure 2: Distribution ratios at high metal concentrations (1.9-2 M) and high EDTA concentrations (0.75-0.8M) for tricaprylmethylammonium nitrate. The variations are due to the pH modifications. The concentration of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity.

Figure 3: Separation factors at high loading (>93% of 2 M) and EDTA concentration (0.75-0.8M), the variation is due to 6M NH₃ additions to modify pH, in a 6 M nitrate matrix (ammonium nitrate). The concentration of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity.

A high rare-earth metal loading (and thereby low additional added nitrate matrix) is desirable as is having as low an EDTA concentration as possible while maintaining a high distribution ratio of elements to be extracted together with high separation factors. Increasing the EDTA concentration increases the binding strength of the
aqueous phase for especially the heavy rare earths and this increases the separation factors, however, all distribution ratios are lowered too much at high EDTA concentrations. Based on the experiments with the 2 M mixed rare-earth solution (6 M nitrate), a series of dilutions down to 0.5 M of total metal content were investigated with varying EDTA concentrations utilizing an ammonium nitrate matrix to have a constant 6 M nitrate in the solutions. The pH in the solutions was kept at approximately pH 2. The effect of EDTA concentration on the 0.5 M rare-earth system is shown in Figures 4 and 5. The distribution ratios decrease strongly with the increasing EDTA concentration. All distribution ratios go below 1 already at 0.55 M EDTA. Up to 0.4 M EDTA the distribution ratio of lanthanum remains fairly high and the separation factors versus yttrium and heavy lanthanides such as dysprosium and beyond are approximately 10000 or even higher.

![Figure 4: Distribution ratios at 0.5 M initial metal concentration in a 6 M nitrate matrix (4.5 M ammonium nitrate added). The composition of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity.](image-url)
Figure 5: Separation factor versus lanthanum at 0.5 M initial metal concentration in a 6 M nitrate matrix (4.5 M ammonium nitrate added). The concentration of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity.

The effect of EDTA concentration on a medium metal loaded system at 1 M rare-earth concentration is shown in Figures 6 and 7. The system is similar to the 0.5 M system with the differences that the distribution ratios are lower and the reduction with increasing EDTA concentration is lower. The separation factors are also somewhat lower with the highest being with the highest tested EDTA concentration with separation factors versus lanthanum for heavy rare earths about a factor of 10 lower at 1000. The separation factors are very dependent on the variation of the rare-earth concentration at a constant, high, EDTA (0.8 M) concentration (Figure 8).
**Figure 6:** Distribution ratios at 1 M aqueous initial total metal loading in a 6 M nitrate matrix (3 M ammonium nitrate added). The concentration of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity.

**Figure 7:** Separation factor versus lanthanum at 1 M initial metal loading in a 6 M nitrate matrix (3 M ammonium nitrate). The concentration of the aqueous feed solution is given in Table 2. Only 5 elements are shown for clarity. Separation factors versus EDTA concentration (M).
The rare-earth metal concentrations in the aqueous phase below 1 M at 0.8 M EDTA concentration have very high separation factors, but suffer from too low distribution ratios. The effect on the separation factors versus lanthanum is large, where the middle lanthanides have a separation factor of approximately 10000 at low initial metal concentration (0.75 M). However, the distribution ratio of neodymium has become somewhat too low since it will require many steps to completely extract the neodymium. Raising the nitrate concentration additionally can counteract this, for example, an ammonium nitrate matrix can be used to attain a nitrate concentration above 11 M without precipitation at room temperature.

The experimental results of using the desired high total nitrate concentration (11 M) with a reasonable initial total metal content (1 M after pH adjustments) combined with an EDTA concentration (0.2 M) optimized for an initial separation of material above dysprosium in the lanthanide series are shown in Table 3. Praseodymium and lutetium concentrations in aqueous (Pr) and organic (Lu) phase were below detection limits.
Table 3: Distribution ratios in tricaprylmethylammonium nitrate and using an aqueous phase of 11 M nitrate with a 1 M rare-earth initial metal concentration with a 0.2 M EDTA concentration. 2 h of mixing at 50 °C, phase ratio 2 (O:A).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Distribution ratio</th>
<th>Separation factor (La)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>520</td>
<td>1</td>
</tr>
<tr>
<td>Pr</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nd</td>
<td>42</td>
<td>13</td>
</tr>
<tr>
<td>Sm</td>
<td>6.3</td>
<td>83</td>
</tr>
<tr>
<td>Eu</td>
<td>4.7</td>
<td>110</td>
</tr>
<tr>
<td>Gd</td>
<td>4.1</td>
<td>130</td>
</tr>
<tr>
<td>Tb</td>
<td>2.7</td>
<td>190</td>
</tr>
<tr>
<td>Dy</td>
<td>1.1</td>
<td>480</td>
</tr>
<tr>
<td>Ho</td>
<td>0.5</td>
<td>1100</td>
</tr>
<tr>
<td>Er</td>
<td>0.2</td>
<td>3500</td>
</tr>
<tr>
<td>Tm</td>
<td>0.01</td>
<td>35000</td>
</tr>
<tr>
<td>Yb</td>
<td>&lt;0.01</td>
<td>82000</td>
</tr>
<tr>
<td>Lu</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>0.4</td>
<td>1200</td>
</tr>
</tbody>
</table>

Conclusions
A system for liquid-liquid extraction based on the ionic liquid tricaprylmethylammonium nitrate, has been investigated for rare-earth separations in pure form using trace-level and high concentration of rare earth in nitrate aqueous solutions with and without EDTA. It was shown that high distribution ratios and separation factors can be achieved using this system and that the distribution ratio decreases with increasing atomic number across the lanthanide series. The separation factors were independent of the nitrate concentration and were improved by using EDTA as an aqueous phase complexant to increase the separation factor for the heavier rare earths. The system behaves favourably when the nitrate concentration is maximized due to the need to increase distribution ratios.

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References

Session V-B: REE Occurrences in Europe
EURARE IKMS: An Integrated Knowledge Management System for Rare Earth Element Resources in Europe

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Abstract

The EU-FP7 project EURARE ‘Development of a sustainable exploitation scheme for Europe’s Rare Earth ore deposits’ will develop an operational data management distributed system based on high-level interoperability standards. Using advances made in EU-FP7 former projects such as OneGeology-Europe, ProMine and EuroGeoSource, ongoing projects like Minerals4EU in terms of database structure, harvesting systems, web services, metadata management, and integration of non-structured information, and InGeoCloudS project in terms of cloud computing, EURARE will contribute to implement the standards of a European geoscientific data infrastructure defined in the EU-FP7 EGDi-Scope project. The objective is to develop an Integrated Knowledge Management System (IKMS) allowing to easily combine rare earth elements (REE) information related to primary and secondary mineral resources and to provide end-users with all the available information from primary sources to new processing techniques and to waste streams. The IKMS will thus be designed as a fully-fledged extension of the EU-MKDP (EU-Minerals Knowledge Data Platform) currently under development within Minerals4EU and which aims to become the future European Mineral Resources (s.l.) data infrastructure. This assures an effective and sustainable system designed for facilitating data updates and maintenance and allowing a full access to information related to the whole REE resources value chain.

1 – Introduction

Data related to raw materials, either metallic, industrial or construction materials, primary or from wastes (mining and industrial) are, most of the time, available in Europe. However, they are often scattered amongst a variety of institutions, including governmental agencies, universities, NGOs and industries. These data are often stored in databases with their own design/architecture and vocabulary, making any attempt of merging – even partially - in view of a compilation difficult and time consuming. The problems regarding availability, quality, organization, accessibility and sharing of data
are common to a large number of policies and are experienced across the various levels of public authorities. Solving these problems requires measures that address exchange, sharing, access and use of interoperable spatial data and services both at national and European levels. This is the aim of the INSPIRE Directive\(^1\), but its implementation in the Member states is just starting and achieving those objectives remains a major challenge.

The development of the IKMS (Integrated Knowledge Management System) aims to give a simplified, user-friendly and efficient access to all available and new data related to REE (Rare Earth Elements) from national geological surveys, scientific institutes and universities, relevant industries and professional organizations, as well as from former European projects such as ProMine\(^2,3\) (information on both mineral deposits and anthropogenic concentrations resulting from mining and downstream activities) and EuroGeoSource\(^4,5\) (information on energy and mineral resources, extraction locations, production, reserves). The system is also designed to accommodate and manage semi- and non-structured data (e.g., syntheses and statistics in the form of graph charts, time-series related to reserves and resources, secondary resources and exploration, European REE market survey and raw material demand, REE resource exploitation technologies including ore beneficiation, extraction technologies, end product development and waste management practices...).

The role of the IKMS is to provide the end-user with a seamless access to the whole value chain from REE deposit exploration, mining and extraction of ore, beneficiation and extraction technologies to treatment of end-of-life products and the generation of "new" materials, with the ability to combine all spatial and non-spatial pertinent information in a single reference system.

2 - IKMS general architecture

The principles of the IKMS architecture follow the Implementing rules of the European INSPIRE Directive\(^1\) to make data and services interoperable across Europe over a distributed infrastructure.

The open architecture (figure 1) defines various components connected together to build the IKMS, taking into account state-of-the-art developments to enhance the performance, stability, sustainability and user friendliness of the system. The connections between the components are specified by standardized interfaces.

The main components of the IKMS architecture are the followings:

- Data on primary and secondary resources from databases provided by geological surveys and former European projects such as ProMine and EuroGeoSource.
These data are delivered through INSPIRE compliant web services and according to INSPIRE (plus extensions) data model\(^6\) and ERML v.2 data model\(^7,8,9,10,11\).

- A system which gives access to available pertinent layers (e.g. geological, geochemical, geophysical, geographical, land use maps...) provided as interoperable services that are registered in a metadata catalogue (accessible via an INSPIRE discovery service).
- New data and information delivered during the project by other work packages (statistics analyses, analyses of REE supply and demand in the EU, stocks, flows, including trends in what products are put on the market and their composition, analyses of the composition of waste products and wastes arising from pre-processing and their geographic location in EU) in various formats will be accessible through the portal. This applies also to any 'open data' of interest for the project. This semi- or non-structured information will be enriched by the provider with a metadata record (e.g., Dublin Core type, see below), then processed and indexed, first extracting relevant information from the documents (e.g., named-entity recognition on atomic elements such as names of locations, expressions of time, thematic specific terms...), then classifying this information according to three facets (spatial, temporal and thematic) and creating indexes for each facet. The way to display the list of selected documents will take into account these three facets.
- Besides a map viewer, the IKMS also includes a search engine for all data, layers and documents delivered by the project and all external pertinent documents.

3 – IKMS detailed architecture

In order to increase the value of the work done in former EU-FP7 project, and also to minimize new developments, it was agreed to reuse the Central Database of the EuroGeoSource project in EURARE. To achieve this goal, there was a need to both update the structure of the database to be ERML 2.0 compliant, and add the support of wastes and chemical analyses. There was also a need to update the database to use the final code lists (or vocabularies) coming from INSPIRE MR specifications which were themselves improved and validated at an international level by the International Union of Geological Sciences (IUGS), Commission for the Management and Application of Geoscience Information (CGI) and the Geoscience Terminology Working Group (GTWG). Finally, the EuroGeoSource cookbook used to help the partners to serve their data has been updated accordingly to the new structure of the database.
3.1 - A professional architecture

The IKMS adopted a professional architecture with a harvesting system and a diffusion system (figure 2). The system is divided into three parts:

- The national level from which ERML 2.0 compliant WFS’ (Web Feature Service) deliver data to the harvesting system either from (already) EuroGeoSource structured databases or directly from other data sources in each country;
- The central harvesting system which regularly reads data from the national WFS’ and stores it in the Harvesting Database. Data is subsequently being delivered to the central diffusion system through a database synchronization mechanism. The Harvesting Database is optimized towards reading data from the national level and delivering this data to the diffusion system;
- The central diffusion system which is updated with data from the harvesting system at regular intervals and makes this data available to users through the IKMS web portal. The Diffusion Database has specific optimization to offer the better experience to the user for the delivery of the data and the computation of on-demand services.

The Information Factory is a software component able to process data (indexation, filtering, descriptive/exploratory statistics computation, automatic report generation...).

3.2 - The national level provider system

Each participating survey will have a National Provider Database which will have the same architecture as the Central Harvesting Database. This database is a PostGreSQL database, which build upon the schema that was used in the EuroGeoSource project, extended by the requirements from EURARE (including mining wastes and geochemical analyses). This Provider Database will contain the data of a survey that was mapped from that survey’s own database using the INSPIRE vocabulary defined in the code lists and data types. This mapping can be done using an ETL (Extraction-Transformation-Loading) tool such as GeoKettle. The data from this database will then be transformed to an INSPIRE compliant web feature service (WFS) using the DeeGree3 framework and toolstack.

3.3 – The harvesting system

The harvesting procedure is based on an updated EuroGeoSource harvesting procedure. The harvesting from the National Provider/project WFS’ is done with an ETL tool run in a scheduled job. Aggregation and other manipulation of data in the
harvesting system, if needed, will be performed by procedures within the PostGreSQL-database.

The possibility to set up an incremental harvesting system, which would avoid a total refreshment of harvested data, is still under consideration. The problem here is not of a technical nature but depends on the fact that some data may not have a time stamp.

3.4 – The Harvesting Database and the INSPIRE MR data model

The Harvesting Database is built by extending the existing EuroGeoSource Central Database with new tables. Additions and changes to the INSPIRE MR data model include:

- the Mining Waste extension from INSPIRE, and the modification of the Earth Material feature used in EuroGeoSource in order to include other materials;
- parts of INSPIRE Draft Guidelines for the use of Observational Measurements and Guidelines for storing geochemical measurements of Earth Material specimens;
- the Mined Material part of the Mine extension from INSPIRE v.3;
- the Supergene Processes from the Occurrence extension from INSPIRE v.3.

The delivery of data from the harvesting system to the diffusion system is carried out by sending SQL update scripts.

3.5 - Vocabularies

Vocabularies used in EURARE are based on INSPIRE MR code lists. These code lists, since their initial publication in the Data Specification on Mineral Resources – Draft Guidelines\(^6\) have been submitted to the IUGS/CGI/GTWG (cf. supra) for validation at the international level and have thus been reworked and improved. During this process, it was ensured that all the needs of the EURARE project regarding REE were taken into account. This led to the improvement – before their final acceptance - of several code lists such as the Commodity Code Value, the Deposit Group and the Deposit Type code lists.

3.6 – The Diffusion Database

The Diffusion Database will be a copy of the Harvesting Database, which will be specialized for data delivery and services that carry out computations based on the stored data. This database will be kept updated with the Harvesting Database using database synchronization. This synchronization will rely on SQL scripts forwarded from the Harvesting Database to the Diffusion Database. The specialization of this database will aim to optimize the response time of the services proposed to the users.
The services on top of the Diffusion Database are:

- Simple map visualizations using WMS (Web Map Services).
- EURARE’s dedicated services: these services are described in a dedicated paragraph below.
- Data download: in some case (and depending on the access rights to the data) the data will be available for download so that they can be processed in other applications (e.g., desktop GIS...).
- Search facilities: these facilities will allow the user to search in the whole database and documents.

3.7 – The non-structured data

Beside the Diffusion Database, an additional interface will allow experts to feed the knowledge base with non-structured data. These non-structured data can be of different types (reports, synthesis notes, thesis...). This interface will allow the expert to add a document (the document will be part of the IKMS and retrievable within the IKMS) or a link to an existing document in some place accessible via the Internet (the document will stay on its original server; the end-user will have to follow a link to retrieve it). To be able to integrate it into the knowledge base, the expert will have to include metadata to this document. These metadata will be based on Dublin Core (http://dublincore.org/) with a specific extension for EURARE (at least quality of the data). Dublin Core Metadata Element Set has 15 elements covering the most important properties to describe a document (title, creator, subject, coverage – temporal or geographical...). These metadata will then be used in the search facilities to retrieve the documents.

3.8 – The search facilities

The search facilities will be based on a search engine indexing the Central Diffusion Database, the documents corpus (non-structured data) and some external databases (if any). A user interface will allow the end-users to retrieve data from the whole IKMS using a simple input (Google-like search, a simple sentence will search in the whole IKMS), or using some specialized interfaces (search specific concepts using their main attributes). Almost all the indexed concepts will have a geographic and temporal extents (coming from INSPIRE MR/ERML for the Diffusion Database, coming from Dublin Core metadata for the documents). These extents will allow the user to retrieve the most accurate response for his search.

3.9 – EURARE’s dedicated services

In order to answer the end-users most common requests, some specific calculation services will be set up for EURARE on top of the Central Diffusion Database. As it is difficult to include LREE and HREE in the Commodity Code Value code list, a service can
be developed which will classify each deposit as a HREE or a LREE deposit, taking into account the main commodity, the second one, etc. This would, for instance, allow plotting deposits on a map with distinct symbols (HREE or LREE), which could be useful for end-users as both groups of REE have different industrial applications. It would also be possible to do this from the geological or metallurgical point of view, as both classifications are not similar. Similarly, a service could also calculate the ratio LREE/HREE, provided that available data is accurate and numerous enough. A service can also be set up for plotting simultaneously known REE deposits (having REE among the main commodities) and deposits containing REE (REE present, but (totally) subordinate). For the latter ones, the selection can be made based on the presence of one or several REE containing mineral(s) in the paragenesis and/or in the mineralogy. This could possibly help to better define provinces or districts.

Finally, both harvesting and diffusion systems will be self-contained systems that can easily be moved to other installations/platforms. More particularly, the project will investigate how platforms like InGeoCloudS could be exploited for the system. This work will be realized in close collaboration with the EGDI-Scope and InGeoCloudS projects.

4 - Conclusion
The present work does not only represent an advance in terms of implementation of a distributed architecture and management of structured, semi- and non-structured data related to REE. It also contributes to the implementation of a European Mineral Resources Data Infrastructure and to bring concrete answers to several recommendations made by the European Commission. The IKMS contributes to the improvement of the standardization of mineral resources data across participating organizations, as suggested in the WP3 of the EC Communication “Making raw materials available for Europe’s future well-being proposal for a European innovation partnership on raw materials” (COM(2012) 82 final) and to the improvement of their availability. It also contributes to implementing land-use planning best practices as suggested in the relevant report by Enterprise and Industry Directorate General (http://ec.europa.eu/enterprise/policies/raw-materials/files/best-practices/sust-full-report_en.pdf). The IKMS outputs will be appropriate for use at a variety of scales, from local/regional land use planning up to the pan-European level. It allows better communication with the general public and specific stakeholders within the mineral sector and facilitates more balanced and well-informed debates and decisions related to the raw materials (and notably critical ones) non-energy extractive industry. Finally, it contributes to the enhancement of minerals role and related industrial technologies for competitive growth as part of the Europe 2020 Strategy.
Figures and captions

Figure 1: Simplified architecture of the EURARE IKMS (Integrated Knowledge Management System). The system is designed to accommodate both structured data from existing databases (data produced by geological surveys or external providers) and semi- or non-structured information produced by other work packages.
Figure 2: The IKMS detailed architecture showing the Harvesting Database, the synchronization process with the Diffusion Database, the Information factory and the indexation process of both structured and semi- and non-structured data. Note the possible use of Excel-type portrayals for feeding project databases.

References


REE DEPOSITS AND OCCURRENCES IN GREENLAND

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Abstract

The Greenland REE potential is considered excellent, consisting of three giant deposits and several smaller deposits in addition to favourable geological settings for undiscovered REE-occurrences. In South Greenland, the main REE occurrences are related to the Mesoproterozoic alkaline intrusions of the Gardar Province, including three world-class deposits: (i) Kvanefjeld and (ii) Kringlerne both hosted by the Ilímaussaq intrusion, and (iii) the Motzfeldt Sø deposit associated with the Igaliko Complex. In West Greenland, the REE occurrences are mainly related to carbonatite intrusions e.g. the Sarfartoq, Qaqarssuk and Tikiussaq intrusions, but some smaller occurrences also exist at Niaqornakavsak, Attu and Nassuttooq. In the Caledonian fold belt of East Greenland, occurrences are related to quartz veins in Bjørnedal, as well as a palaeoplacer deposit at Milne Land.

Introduction

Greenland comprises several large REE deposits in various geological settings. The largest deposits are hosted in peralkaline intrusions related to the Gardar Province in South Greenland, including the deposits around Kvanefjeld, Kringlerne, and Motzfeldt Sø. Additionally, three carbonatite deposits are known from the West coast, and quartz veins in Bjørnedal and one palaeoplacer deposit (Milne Land) are located in East Greenland (Figure 1). An overview of the REE-deposit types and main REE-minerals are listed in Table 1. Additionally, Greenland holds potential for undiscovered REE deposits related to carbonatite magmatism, alkaline intrusions, pegmatite settings, IOCG mineralising systems, and palaeoplacer environments1,2.

South Greenland

The Mesoproterozoic Gardar province in South Greenland is an intracratonic rift province of sandstones, and a variety of volcanic and plutonic igneous rocks of alkaline and peralkaline affinity. Of the intrusions in the province, the most important economic REE deposit include the Ilímaussaq intrusion (1160 Ma), and the Igaliko Nepheline Syenite Complex (1273 Ma), hosting the Kvanefjeld and Kringlerne REE
deposits, and the Motzfeldt Sø REE deposit, respectively. In addition, the Gardar province also encompasses the minor REE carbonatite occurrence at Grønnedal-Ika.

The Ilímaussaq intrusion is largely emplaced during block subsidence and formed by three pulses, of which the third pulse formed a layered series of nepheline syenite, enriched in REE, U, Nb, Ta, Zr, Zn and F. The Ilímaussaq intrusion covers an area of 8 km x 17 km and hosts two world class REE deposits: (i) Kvanefjeld, an intermediate series sandwiched between roof and floor series, which consist mainly of lujavrites, and (ii) Kringlerne, the bottom cumulates of kakortokite.

The Kvanefjeld multi-element deposit is an accumulation of igneous rocks from the central part of the Ilímaussaq intrusion. The bulk of the REE and the U is associated with lujavrite rocks containing disseminated steenstrupine, lovozerite and an unnamed mineral species. Greenland Minerals and Energy Ltd. (GME) has been the license-holder since 2007, and reports\(^3\) the indicated JORC compliant resources of Kvanefjeld to be 437 Mt ore grading 1.1 % TREO, hence containing 4.8 Mt TREO (0.18 Mt HREO), 263 Mlbs U\(_3\)O\(_8\), and 1 Mt Zn. In addition, they have located and assessed two other lujavrite bodies in the vicinity, the Sørenszone and Zone 3. However, the proposed mining project is focused on the Kvanefjeld deposit. The deposit will be exploited as an open pit mine, with ore beneficiation at an adjacent plant, extracting sphalerite by flotation followed by hydrometallurgical leaching of steenstrupine and recovery of the uranium and REE. GME anticipate annual production to be in the range of 3 Mt ore resulting in 33,000 ton TREO (equivalent to 3,400 ton Nd\(_2\)O\(_3\) and 300 ton Dy\(_2\)O\(_3\)), 1.8 Mlbs U\(_3\)O\(_8\) and 6,636 ton Zn. The feasibility report is in progress.

The Kringlerne multi-element deposit is hosted in agpaitic kakortokite, and consists of a total of 29 exposed cyclic layers with a total thickness of about 200 m, made up by arfvedsonite dominated kakortokite, eudialyte dominated kakortokite, and a nepheline-feldspar dominated kakortokite. Eudialyte, the main economic mineral, is enriched in REE-Zr-Nb-Ta. TANBREEZ is the current license-holder, and they report\(^4\) the inferred JORC-compliant resource to be at least 4,300 Mt grading 0.65 % TREO, 0.2 % Nb\(_2\)O\(_3\) and 1.8 % Zr\(_2\)O\(_3\) equaling 28 Mt TREO. Their proposed mining project involves an open pit mine near the fjord, hauling the ore to a nearby beneficiation plant, where they will produce three products: (i) eudialyte concentrate (REE, Nb, Zr); (ii) feldspar concentrate, and (iii) arfvedsonite concentrate, all to be shipped for further processing and/or use outside Greenland. Planned annual production is set at\(^5\) 500,000 ton ore, equal to 3,250 ton TREO (equivalent to 400 ton Nd\(_2\)O\(_3\) and c. 90 ton Dy\(_2\)O\(_3\)) and 9,000 ton Zr\(_2\)O\(_5\). The feasibility report is in progress.

The Motzfeldt Sø REE deposit is part of the Motzfeldt Centre, which in turn is one of the intrusions of the Igaliko Nepheline Syenite Complex. It contains extensive U-Nb-Ta-Zr-REE mineralisation\(^6,7\). Significant Ta-Nb-enriched zones relate to altered syenite, minor pegmatite and diorite dykes and high grade REE intersections are related to pegmatites at depth. Presently, RAM Resources Ltd. has licensed the area and reports\(^8\)
a resource estimate of 340 Mt grading 0.26 % TREO, 0.19 % Nb₂O₅, 0.012 % Ta₂O₅ and 0.46 % ZrO₂. A scoping study is in progress.

**West Greenland**

West Greenland possesses a number of carbonatite associated REE deposits intruded between Neoproterozoic and Jurassic. The most important of those, in terms of REE resources, are Sarfartoq, Qaqarssuk, and Tikiussaq. These carbonatites are located in southern West Greenland intruded into the Archaean basement of the North Atlantic Craton. In addition, West Greenland hosts minor REE occurrences at Niaqornakavsak, Attu and Nassuttooq.

The Sarfartoq carbonatite intrusion is located on a Precambrian thrust zone and intruded 560 ± 13 Ma ago⁹,¹⁰, during the opening of the Iapetus Ocean. The host rock consists of orthogneiss with schlieren of amphibolite. The complex has an ellipsoidal shape and covers about 90 km², of which 15 km² are intrusive carbonatites. The core of the complex consists of rauhaugite with schlieren of sövite and beforite dykes, surrounded by a Na-type fenite zone with aegerine- and pyrochlore-bearing rocks. The carbonatite contains REE-bearing minerals in veinlets of dolomite and REE-carbonatite and in shear zones with thorium, uranium, K-feldspar alteration and limonitisation¹¹. The most common REE-minerals are synchysite and zhonghuacerite, which are relatively enriched in LREE¹², most notably Ce, La and Nd. Furthermore, ancylite, burbankite and Sr-REE barite were observed¹³. Hydrothermal activity caused an enrichment of niobium in the carbonate veins and shear zones, which have been drilled in the past. Hudson Resources Ltd. currently holds the license of the area and reports resource estimates that include indicated NI 43-101 compliant resources of 5.9 Mt averaging 1.8 % TREO and an additional inferred resource of 2.5 Mt averaging 1.6 % TREO, based on a 1 % cut-off grade¹²,¹⁴.

The Qaqarssuk carbonatite (Qeqertaasaq) complex consists of carbonatite ring-dykes that are elliptical to semi-rectangular in shape and intruded into the Archaean basement at 165.7 ± 1.9 Ma⁹,¹⁰. The carbonatite covers an area of 15 km² and is surrounded by fenitised basement. The ring-dykes consist of sövite, olivine-sövite, and dolomite carbonatite. They are cut by late-stage sövite veins, REE-carbonatite veins, ferrocarbonatite and lamprophyre dykes¹⁵. The sövites contain increasing amounts of silicate minerals and inclusions of fenitised basement away from the centre of the complex. The fenites are composed of albite, alkali amphibole, and alkali pyroxene¹⁶. The major REE minerals in the complex are ancylite, burbankite, huanghoite and qaqarssukite. NunaMinerals A/S holds the license for the area and report¹⁷ that surface sampling and trenching have yielded up to 13.2 % TREO within the late-stage carbo-hydrothermal REE veins, and that drilling demonstrated that the REE veins are up to 4.5 % TREO. Metallurgical flow sheets are currently being defined.
The Late Jurassic Tikiusaq carbonatite complex was discovered in 2005\textsuperscript{18}. The presence of the carbonatite was predicted by a study of regional stream sediment geochemistry and aeromagnetic data. The complex consists of a central intrusive carbonatite surrounded by a fenite zone with carbonatite and aillikite dykes, and the main REE-mineral is bastnaesite. The exposed carbonate sheets cover 2 km x 3 km, and the alteration zone extends up to 14 km in diameter. Remote sensing data suggest that a massive carbonatite is hidden below the glacial terraces. Both magmas have common origin within carbonated upper mantle source\textsuperscript{19}. The 165-150 Ma carbonatite intruded during the opening of the Labrador Sea. Apart from REEs, the carbonatite complex hosts P, Nb and Ta. The highest grade REEs are associated with a thorium anomaly. NunaMinerals A/S holds the license for the area and reports up to 9.6 % TREO in a carbonate float\textsuperscript{17}.

The Niaqornakavsak REE deposit was discovered in 2007 by Avannaa Resources who still holds the license of the area. The mineralisation is hosted in Early Proterozoic metasediments and metavolcanic of the Karrat Group, situated in the Karrat Isfjord region. The mineralisation is a lithological distinct horizon of banded carbonates within an amphibolite unit. The horizon strikes 1.5 km and dips 32 degrees. The mineralised body is estimated to contain tens of millions tons of ore. Drill intersections indicate that TREO+Y typically varies between 0.8 and 1.5 wt. % with some layers containing up to 1.9 wt. % with an average of 1.03 wt. %. The REE`s are mainly hosted by bastnaesite, monazite, allanite and other REE silicates\textsuperscript{20}. The Niaqornakavsak bulk samples indicate an average TREO+Y of 1.36 wt. % of which the average HREO+Y content is 13.06 %. A metallurgical analysis and flow sheet development is in progress.

**East-Greenland**

In the Caledonian fold belt of East Greenland, a couple of occurrences exist in quartz veins in Bjørnedal, in a palaeoplacer deposit at Milne Land and in an alkaline intrusion in the Gardiner Complex.

Nb-REE-bearing types of mineralisation occur in the Kap Simpson complex in Bjørnedal on Traill Ø. The mineralisation occurs in course-grained quartz veins intruding Jurassic/Cretaceous shales, siltstone and sandstones. The veins are up to 30 m long and 15 cm wide and contain minor amounts of Nb and REE-bearing minerals columbite, euxenite, samarskite, fergusonite, monazite and bastnaesite. Selected samples contain up to 3.2 % Nb and 3 % REE, but the average content is not reported\textsuperscript{21}.

In East-Greenland, the Jurassic placer deposit on Milne Land is forming another source for REEs. The deposit, placed within the Mesozoic basins in central East Greenland, formed during the opening of the North Atlantic Ocean. The placer consists of heavy mineral-bearing arkosic sandstones and breccias that are rich in zircon, monazite, Ti-
minerals and garnet. The units form the lowermost 20 m of the Charcot Bugt Formation, which rests unconformably on Mesoproterozoic migmatic granite. The best outcrops occur on Hill 800, where these sedimentary rocks are 40-50 m thick and are more than 500 m in diameter. CGRG Ltd. currently has the license for the area and is exploring for Mo-Zr-REE-Ti.

**Conclusion**

The Greenland REE potential is considered excellent including several known deposits, as well as favourable geological settings for undiscovered REE-occurrences such as alkaline intrusions, pegmatite settings, carbonatites and IOCG mineralising systems. Currently, two giant deposits that have reached advanced stage of development, plan to enter operation before 2018.

![Known REE deposits/occurrences in Greenland](image)

**Figure 1:** Known REE deposits/occurrences in Greenland
Table 1: Deposit types and REE-minerals of the Greenland REE-occurrences

<table>
<thead>
<tr>
<th>Occurrence</th>
<th>REE-deposit type</th>
<th>Main REE minerals</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attu</td>
<td>Granitic</td>
<td>Allanite</td>
<td>(Ce, Ca, Y, La)(_2) (Al, Fe(^{3+}))(_3) (SiO(_4))(_3) (OH)</td>
</tr>
<tr>
<td>Bjørnedal</td>
<td>Granitic</td>
<td>Eu xenite, Samarskite, Fergusonite, Monazite, Bastnaesite</td>
<td>(Y, Ca, Ce, U, Th)(_2) (Nb, Ta, Ti)(_2) O(_6) (YFe(^{3+})+Fe(^{2+})+U, Th, Ca)(_2) (Nb, Ta)(_2) O(_8) REENbO(_4) (Ce, La)PO(_4) (Ce, La, Y)CO(_3)F</td>
</tr>
<tr>
<td>Gardiner</td>
<td>Alkaline</td>
<td>Perovskite, Apatite</td>
<td>CaTiO(_3) Ca(_5) (PO(_4))(_3) (F, Cl, OH)</td>
</tr>
<tr>
<td>Grønnedal-Ika</td>
<td>Carbonatite</td>
<td>Bastnaesite</td>
<td>(Ce, La, Y)CO(_3)F</td>
</tr>
<tr>
<td>Kringlerne</td>
<td>Alkaline</td>
<td>Eudalyte</td>
<td>Na(_{15}) Ca(_6) (Fe, Mn)(_2) Zr(_3) SiO(_2) (OH, H(_2)O)(_3) (Si(_3) O(_9))(_2) (Si(_3) O(_2))(_2) (OH, Cl)(_2)</td>
</tr>
<tr>
<td>Kvanefjeld</td>
<td>Alkaline</td>
<td>Steenstrupine, Lovozerite</td>
<td>Na(_{14}) REE(_6) (Mn, Fe)(_3) (Th, U, Zr) (Si(_6) O(_18))(_2) (PO(_4))(_7) 3H(_2)O Na(_2) Ca Zr REE (H(_4) Si(_6) O(_18)) H(_2)O</td>
</tr>
<tr>
<td>Milne Land</td>
<td>Palaeoplacer</td>
<td>Monazite</td>
<td>(Ce, La) PO(_4)</td>
</tr>
<tr>
<td>Motzfeldt Sø</td>
<td>Alkaline</td>
<td>Pyrochlore, Bastnaesite, Monazite, Eudalyte</td>
<td>(Na, Ca)(_2) Nb(_2) O(_6) (OH, F) (Ce, La, Y) CO(_3)F (Ce, La) PO(_4)</td>
</tr>
<tr>
<td>Nassuttoq</td>
<td>Granitic</td>
<td>Monazite</td>
<td>(Ce, La)CO(_3)F</td>
</tr>
<tr>
<td>Niagornakavsk</td>
<td>Carbonatite?</td>
<td>Bastnaesite, Monazite, Allanite</td>
<td>(Ce, La, Y)CO(_3)F (Ce, La) PO(_4) (Ce, Ca, Y, La)(_2) (Al, Fe(^{3+}))(_3) (SiO(_4))(_3) (OH)</td>
</tr>
<tr>
<td>Qaqarssuk</td>
<td>Carbonatite</td>
<td>Ancylite, Burbankite, Huanghioite, Qaqarssukite</td>
<td>Sr(Ce, La) (CO(_3))(_2) (OH) H(_2)O (Na, Ca)(_3) (Sr, Ba, Ce) (CO(_3))(_2) BaCe (CO(_3))(_2) F Ba(Ce, REE) (CO(_3))(_2) F</td>
</tr>
<tr>
<td>Sarfartoq</td>
<td>Carbonatite</td>
<td>Synchysite, Zhonghuacirit e</td>
<td>Ca(Ce, La, Nd, Y) (CO(_3))(_2) F Ba(_2) (Ce, La, Nd) (CO(_3))(_3) F</td>
</tr>
</tbody>
</table>
References

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The Motzfeldt Centre of the Igaliko Nepheline Syenite Complex, South Greenland - A major resource of REE elements

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Abstract

The Motzfeldt Centre (1,273 ± 6 Ma) is one of four major alkaline centres belonging to the Igaliko complex, part of the Mid-Proterozoic Gardar province of South Greenland. The Centre covers an area of approximately 150 km² with excellent 3-dimensional exposure. The Motzfeldt Centre is made up of multiple intrusions of syenite. The syenites were emplaced as two main igneous phases into the Proterozoic Julianehåb batholith and the unconformably overlying Gardar supracrustal rocks. The apparent intrusion mechanism was a combination of block stoping, ring fracture and partial ring dyke formation. The oldest igneous phase, the Motzfeldt Sø Formation, underwent an extreme in situ differentiation, which resulted in the formation of peralkaline residues rich in volatile and incompatible elements. The peralkaline residues gave rise to a complex of late peralkaline sheets of microsyenite and pegmatite, and pervasive hydrothermal alteration with associated Th-U-Nb-Ta-Zr-REE mineralization which increases in the intensity towards the margins, and especially towards the roof of the intrusions.

The highest enrichment of REE and Y and the relative enrichment of HREE are confined to the peralkaline sheet complex in the roof zone of the intrusion. The volumes of the peralkaline microsyenite with 0.6 – 1.1% TREO is huge and can be estimated to a minimum of 80 million tons.

Introduction

High-field-strength-elements (HFSE) such as Zr, Hf, Nb, Ta, Y, REE, Th and U are often enriched in alkaline rocks where a substantial volume of the world's strategic reserves...
of these elements are found. The mid-Proterozoic Gardar province in South Greenland (Fig. 1) representing the products of repeated rift-related alkaline magmatism\textsuperscript{9,10} in the Proterozoic Ketilidian (1,900 -1,700 Ma) and Archaean rocks\textsuperscript{9,10} during the period ~1,300 – 1,140\textsuperscript{6,7,8} Ma. There are approximately ten major intrusive complexes of alkaline rocks of Gardar-age in southern Greenland. The intense enrichment of the HFSE-elements in the agpaitic intrusive units of Ilímaussaq intrusion has been known and evaluated since 1971\textsuperscript{15}. The extensive mineralisation of the HFSE-elements in the Motzfeldt Centre of the Igaliko Complex was discovered in late 1970’s\textsuperscript{4} and Centre has been a target for geological mapping and exploration for Nb and Ta \textsuperscript{13,14}.

Geology of the Motzfeldt Centre

The Motzfeldt Centre (Fig. 2) appears to be a classic example of central-type alkaline complexes which developed which developed through the successive emplacement of syenite guided by combination of ring fractures and block subsidence.

Figure 1: Geological sketch map of South Greenland\textsuperscript{1}. The location of the Igaliko Complex, Motzfeldt Centre and Ilímaussaq intrusion is highlighted.
The syenite units of the main igneous phase originally comprised a circular body about 18 km in diameter having a shape of “bell jar”. The contact relationships between the syenites and the syenites/basement rocks in indicate that the emplacement of the syenites took place passively via permissive stoping.

The Motzfeldt Sø Formation (MSF) is the oldest unit of the centre and now occupies its outer part. The MSF has been divided into two major concentric zones: namely inner Nepheline syenite and outer altered syenite. No evidence of these zones as separate intrusions has been found. The MSF hosts a conspicuous sheet complex of pegmatite/aplite and peralkaline lujavrite and peralkaline microsyenite.

The Flinks Dal Formation (FDF) occupies the core of the MRS and includes three major intrusions of phonolitic composition.

The present exposure of syenites is an intricate combination of faulting and topography. The Centre was affected by two major sets of vertical or nearly vertical faults, one striking NE-SW (older) and another approximately E-W (younger). The fault sets display both vertical and horizontal component.

The younger E-W striking faults are characterised by movements in sinistral sense. The Flinks Dal Fault (Fig. 2) traverses the whole centre with a horizontal component of about 6 km.

The present altitude of the Eriksfjord Formation/basement unconformity provides a means to evaluate the magnitude of the vertical movements along the faults. The Flinks Dal Fault has the most dramatic downthrow of a minimum of 600 metres to the north.

**The Motzfeldt Sø Formation – mineralisation of HFSE-elements**

The texturally and mineralogically highly variable units of the Motzfeldt Sø Formation (Fig. 3) contain exceptionally high concentrations of Th, U, Nb, Ta, Zr and REE and volatile components such as F and H2O. Within the inferred roof zone (fig. 4) the diversity of rock types is most extreme with the highest enrichment of HFSE.

The rock types of the MSF, their mineralogical and chemical characteristics manifest and extreme internal differentiation of the phonolitic (?) magma. Along with the progressive crystal fractionation the incompatible elements and volatile components were increasingly concentrated at the top of the chamber. The build-up of the volatiles must have affected the physical and chemical properties of magma/fluid. The peralkaline magma was able to dissolve large amounts of volatiles12 and there may have been a gradual transition into a hydrothermal fluid. The formation of the peralkaline sheet complex could be related to a formation of such a fluid phase.

The MSF and the peralkaline sheets complex are characterised by the pervasive hydrothermal alteration associated with the subsolidus evolution of the MSF. The textural relationships of the minerals indicate that the migration involved a continuous readjustment (precipitation/leaching) of the mineral phases with the proceeding
hydrothermal activity. The proceeding hydrothermal activity was accompanied by the relative and absolute enrichment the HFSE.

Figure 2: Geological map of Motzfeldt alkaline centre (after Bradshaw\textsuperscript{2}; Jones\textsuperscript{3}; Tukiainen \& al.\textsuperscript{4}). The great numbers of dykes, predominantly alkali trachytes of the late-Gardar dyke swarm are omitted for the sake of clarity. The localities referred in the text are highlighted:

The extent and the intensity of the Th-U-Nb-Ta-Zr-REE mineralisation are well outlined by the high resolution airborne gamma spectrometer survey\textsuperscript{4}.

The mineralogy of the HFSE in the MSF is complex. The REE are dominantly hosted by REE–carbonates, pyrochlore, monazite and eudialyte (table 1.)

The peralkaline sheet complex was sampled in selected mineralised localities as vertical profiles traversing from 20 to 200 metres of ground with a sampling density of reconnaissance character (table 2.).
Reserve estimates

The peralkaline sheet complex

The peralkaline sheet complex of the Motzfeldt Centre constitutes a huge reserve of Zr in the class 1-2 % ZrO₂. The extent and the intensity of the Th-U-Nb-Ta-Zr-REE mineralisation is well outlined by the high resolution airborne gamma spectrometer survey. Within the inferred roof-zone, the diversity of rock types is most extreme and roof zone hosts the highest concentrations of HFSE and REE. Large portions of the roof-zone are preserved in North and South East Motzfeldt containing 0.6 - 1.5 % TREO covering 4 and 6 km² of ground, respectively. Assuming that only the topmost 50 meters of peralkaline sheet complex is of interest, the rock volumes in this category are c. 1250 Mt containing 0.6 - 1.5 % TREO corresponding to 75 – 187 million tons of contained REO, respectively.
**Figure 4:** The peralkaline sheet complex of lujavrite and microsyenite in North Motzfeldt. The water table of the lake is 162 metres a.s.l., the mountain top is 1500 metres a.s.l. The MSF roof zone below the Eriksfjord Formation indicated with red colour.

**The MSF altered syenite**

The enrichments of pyrochlore in the MSF altered syenite have been assessed for their economic potential for Ta and Nb. The Aries Prospect of the Ram Resources Limited (Fig. 1) with an exploration potential of 200 – 500 Mt @1800-2200 ppm Nb₂O₅ , 130-160 ppm Ta₂O₅ and 3000-5000 ppm TREO contained both in Pyrochlore (4-6 % TREO) and REE-carbonate (70 % TREO)

The extraction of Ta and Nb from pyrochlore may also yield significant quantities U, Th, Zr and LREE.
**Table 1:** Dominant minerals for Nb-Ta-REE-Zr-Y-U in the MSF (Tukiainen\textsuperscript{11}, 1988)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Nb2O5</th>
<th>Ta2O5</th>
<th>REE\textsubscript{2}O\textsubscript{3}</th>
<th>ZrO\textsubscript{2}</th>
<th>Y2O\textsubscript{3}</th>
<th>UO\textsubscript{2}</th>
<th>ThO\textsubscript{2}</th>
<th></th>
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<tbody>
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<td>Pyrochlore</td>
<td>54.78</td>
<td>1.42</td>
<td>16.1</td>
<td>1.04</td>
<td>-</td>
<td>6.88</td>
<td>0.13</td>
<td>Altered syenite</td>
</tr>
<tr>
<td>Columbite</td>
<td>68.13</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>Bastnaesite</td>
<td></td>
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<td>70.0</td>
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<td></td>
<td></td>
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<td>Zircon</td>
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<td></td>
<td>46.3</td>
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<td></td>
<td>0.7</td>
<td>5.53</td>
<td>50.58</td>
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<tr>
<td>Monazite</td>
<td>63.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.3</td>
<td>Altered syenite</td>
</tr>
<tr>
<td>Eudialyte</td>
<td>2.47</td>
<td></td>
<td>5.68</td>
<td>12.21</td>
<td>-</td>
<td>-</td>
<td>Lujavrite, unaltered</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2:** Content of the HFSE-elements in selected mineralised localities of the peralkaline sheet complex of the Motzfeldt Sø Formation

<table>
<thead>
<tr>
<th>Locality (Map 2)</th>
<th>(\sum\text{CeO}_2\text{LaO}_2\text{Nd}_2\text{O}_3)</th>
<th>Y\textsubscript{2}O\textsubscript{3}%</th>
<th>U ppm</th>
<th>Th ppm</th>
<th>ZrO\textsubscript{2}%</th>
<th>Nb2O\textsubscript{5}%</th>
<th>Ta2O\textsubscript{5}%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geologfjeld</td>
<td>0.1 - 0.3%</td>
<td>0.06 - 0.1%</td>
<td>100 - 500</td>
<td>100 - 600</td>
<td>0.6 - 1.5%</td>
<td>0.2 - 0.6%</td>
<td>0.01 - 0.03%</td>
</tr>
<tr>
<td></td>
<td>Max. 0.9%</td>
<td></td>
<td></td>
<td></td>
<td>Max. 2%</td>
<td>(Max. 1%)</td>
<td></td>
</tr>
<tr>
<td>North East Motzfeldt</td>
<td>0.4 - 1.1%</td>
<td>0.02-0.05%</td>
<td>100 - 200 Max. 1400</td>
<td>200 - 300 Max. 1900</td>
<td>0.9 - 1.5%</td>
<td>0.2 - 0.5%</td>
<td>0.005 - 0.01%</td>
</tr>
<tr>
<td></td>
<td>Max. 2%</td>
<td></td>
<td></td>
<td></td>
<td>Max. 2%</td>
<td>(Max. 1%)</td>
<td></td>
</tr>
<tr>
<td>South East Motzfeldt</td>
<td>0.2 - 0.4%</td>
<td>0.012-0.12%</td>
<td>200 - 866</td>
<td>300-4936 Max. 9000</td>
<td>1.0 - 1.3%</td>
<td>0.2 - 0.3%</td>
<td>0.01 - 0.03%</td>
</tr>
<tr>
<td></td>
<td>Max. 1%</td>
<td></td>
<td></td>
<td></td>
<td>Max. 2%</td>
<td>(Max. 1%)</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

The magmatic differentiation of the Motzfeldt Sø formation resulted in the formation of peralkaline rocks with the exceptional enrichment of HFSE (Th-U-Nb-Ta-Zr, Y-REE) towards the margins and especially towards the roof of the intrusion. The preserved inferred topmost roof-zone of the intrusion in North East and South East Motzfeldt is likely to host a reserve of c. 1250 Mt with the TREO content varying from 0.6 - 1.5 % TREO.

References

ALTERATION OF EUDIALYTE AND IMPLICATIONS FOR THE REE, ZR, AND NB RESOURCES OF THE LAYERED KAKORTOKITES IN THE ILÍMAUSSAQ INTRUSION, SOUTH WEST GREENLAND

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Abstract

The layered kakortokites in the southern part of the Ilímaussaq Intrusion are of great economic interest due to their high concentrations of REE, Zr, Nb and Ta. The prospective metals are largely contained in eudialyte, a complex sodium-zirconosilicate and one of the major cumulus phases. Eudialyte-group minerals are easily extracted from the host rock through magnetic separation, and contain 12 wt% ZrO2, 2% TRE2O3 and 1% Nb2O5 on average. Petrographic investigations show that a large fraction of eudialyte at Ilímaussaq is replaced by complex aggregates of secondary minerals as a result of interaction with late-stage magmatic, presumably Na- and F- rich aqueous fluids. The alteration effectively fractionates the major components into the secondary minerals, producing separate Zr-, Nb and REE-phases, leading to an increased complexity of the mineralisation and potential ore recovery.

Introduction

The Ilímaussaq Complex in Southern Greenland hosts some of the most evolved alkaline rock types in the world and is the type-locality of agpaitic nepheline syenites. The term agpaitic exclusively refers to peralkaline rocks with a molar (Na+K)/Al ratio greater than 1.2, containing complex zircono- and titanosilicates, such as eudialyte- and rinkite-group minerals, instead of common high field strength element-bearing (HFSE) phases like zircon, titanite and ilmenite1,2. Eudialyte represents a prime REE, Nb and Zr resource provided by these rock types. The mineral can be readily separated from other minerals (alkali feldspar, arvedsonite and feldspathoids) by simple magnetic separation and is highly soluble in acids, providing a potential low-cost ore material. Other occurrences of agpaitic rocks are the Khibina and Lovozero complexes in the Kola Peninsula, Mont Saint-Hilaire in Canada, the Tamazeght Complex in
Morocco and Norra Kärr in Sweden. All are characterized by extreme enrichment in alkali metals, halogens (F, Cl, Br) and HFSE (e.g. Zr, Ti, Y, Nb, Ta and REE), and many host exploitable resources of these elements.

The Ilímaussaq Complex has the potential for two types of world-class multi-element magmatic ore deposits; 1) the Kringlerne deposit, studied here, which occurs in cumulates forming the lower part of the intrusion, and 2) the Kvanefjeld deposit in the most evolved lujavrites exposed in the Northern part of the intrusion. The Kringlerne deposit comprises a ~500 m thick series of rhythmically layered amphibole-, eudialyte- and feldspar-rich nepheline syenites (black, red and white kakortokites, respectively), which is currently being explored as a potential REE, Zr, Nb and Ta economic deposit. The resource estimates are 4.3 Bt with an average grade of 1.8 % ZrO₂, 0.2 % Nb₂O₅ and 0.5 % TREO. The enormous tonnages and relatively high proportion of heavy relative to light rare earth elements (HREE/LREE) in eudialyte (approximately 1:3) compared to currently exploited REE deposits, make the deposit especially attractive. Proposed on-site processing involve coarse crushing followed by magnetic separation, producing concentrates of 1) eudialyte, 2) arfvedsonite-aegirine and 3) a mixture of felsic minerals.

Field observations combined with petrographic and electron-microprobe (EPMA) analyses show that a significant amount of eudialyte in the kakortokites has been altered forming a suite of secondary minerals including catapleiite (Na-Zr silicate), aegirine, pectolite, analcime, alkali-feldspar, nacareniobsite-(Ce) (REE-Nb silicate), britholite (REE-phosphosilicate), monazite (REE-phosphate) and pyrochlore (formulas provided in Table 1), previously described in detail by Karup-Møller et al.7,8. The bulk composition of pseudomorphosed eudialyte appears to be preserved, but with major components, notably Zr, REE and Nb, redistributed among the newly formed minerals. The goals of this study are to improve the general knowledge of the relative timing and processes of crystallisation and alteration, the de facto distribution of elements of economic interest and possible implications for beneficiation of the ore.

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>aegirine</td>
<td>NaFe(Si₂O₄)</td>
</tr>
<tr>
<td>arfvedsonite</td>
<td>Na₃(Fe,Mg)₄FeSi₆O₂₂(OH)₂</td>
</tr>
<tr>
<td>analcime</td>
<td>NaAlSi₂O₅H₂O</td>
</tr>
<tr>
<td>pectolite</td>
<td>NaCa₂Si₂O₆(OH)</td>
</tr>
<tr>
<td>eudialyte</td>
<td>Na₂₅Ca₈(Fe,Mn,Na)₃(Zr,Ti)₃(Si, Nb)₂Si₄O₇₂(O,OH,H₂O)₃(Cl,OH)₂</td>
</tr>
<tr>
<td>catapleiite</td>
<td>(Na, Ca)₂ZrSi₅O₉·2H₂O</td>
</tr>
<tr>
<td>zircon</td>
<td>(Zr,REE)SiO₄</td>
</tr>
<tr>
<td>apatite</td>
<td>Ca₅(PO₄)₃(F,Cl,OH)</td>
</tr>
<tr>
<td>britholite-(Ce)</td>
<td>(Ca,Ce)₅(SiO₄,PO₄)₃(OH,F)</td>
</tr>
</tbody>
</table>

Table 1: Selection of relevant minerals mentioned in text
Eudialyte Group Minerals

Eudialyte group minerals (EGM), the most prominent index minerals for agpaitic rocks, encompass a large compositional range and are inferred to crystallise at various stages in the magmatic history<sup>9</sup>. Eudialyte group minerals have a complex structure, with a general structural formula of \( \text{N}_{15-16} \text{M}(1)_6 \text{M}(2)_3 \text{Z}_3 \text{M}(3) \text{M}(4)[\text{Si}_{24} \text{O}_{72}]\text{OH}_2\rightarrow 6\text{X}_2 \), where N, M and Z refer to different crystallographic sites incorporating variable amounts of Na, Ca, Fe, Mn, Sr, REE, Nb, Si, Zr and Ti as well as volatile components (H\(_2\)O, Cl, F, OH)<sup>10,11</sup>. In the kakortokites EGM are generally Fe-rich, approaching eudialyte sense stricto compositions, with a general formula of \( \text{Na}_{15} \text{Ca}_6(\text{Fe,Mn})_3\text{Zr}_3\text{Si}(\text{Si}_{22}\text{O}_{72})(\text{O,OH,H}_2\text{O})_3(\text{Cl,OH})_2 \), with the major part of the REE and Nb situated in the M1 and M3 site, respectively<sup>12</sup>. Owing to their great compositional variability and sensitivity to hydrothermal re-equilibration, EGM typically record late-stage magmatic and hydrothermal processes in agpaitic systems<sup>13-15</sup>. These processes could result in partial or complete decomposition of the eudialyte into complex aggregates of secondary minerals<sup>8,14,15</sup>.

Analytical Methods

Eudialyte and its decomposition assemblages were analysed in approximately 30 samples, including black, red and white kakortokites from layers -11 to +164, using optical microscopy, back-scatter electron imagery (BSE) and wavelength dispersive electron microprobe analyses using a JEOL JXA-8200 at University of Copenhagen. All analyses were run at an acceleration voltage of 15 kV, beam current 15 nA and a beam diameter of 5 or 20 µm, using a set-up similar to that described by Karup-Møller et al. (2010, 2013). Counting times range from 10-60 seconds, depending on the abundance and volatility (Na) of the respective elements. Background counting times were half of the peak counting times.

Petrographic observations

Primary eudialyte description
The eudialyte-group minerals form well-developed idiomorphic crystals with an average grain size of 0.5 - 1 mm. In all three varieties of kakortokite (black, red and white) EGM are part of the early crystallising assemblage\textsuperscript{4,12}. In black kakortokites EGM occur between, or are fully enclosed by arvedsonite crystals. In white kakortokite eudialyte crystals are generally interlocked between gravitationally aligned laths of feldspar and grains of nepheline. Intact EGM exhibit complex sector-zoning, fine oscillatory zoning (sub-\(\mu\)m) as well as concentric core to rim zonation (Fig. 1a). Hourglass sector zoning is present in most crystals and represents a crystallographically controlled feature, presumably caused by preferential incorporation of certain elements on a specific set of growth surfaces\textsuperscript{16}. Sector-zoning is associated with minor differences in Nb and Ce (LREE) contents (< 0.2 wt\%) between light and dark sectors. Rims showing uniformly high or low backscatter-index typically occur along specific faces of primary sector-zoned eudialyte crystals (Fig. 1a). These rims are distinctly enriched or depleted in REE and presumably reflect changes in the REE-budget of the evolving (interstitial) melt in the final stages of crystallisation.

**Alteration paragenesis**

A significant proportion of the cumulus eudialyte was subjected to late-stage replacement reactions. First-stage alteration occurs as irregular replacement or symplectite formation along margins and cracks and is associated with crystallisation of fine-grained anhedral crystals of the Na-zirconosilicate catapleiite (mineral formulas provided in Table 1), as well as \(\mu\)m-sized Ce- and Nb-rich phases. Upon further alteration an increasing volume of eudialyte is consumed until the grain is completely replaced by secondary phases (Fig. 1b,c,d). Relics of eudialyte in some pseudomorphs retained their original composition, although they are locally associated with minor loss of Na and Cl. In pseudomorphs representing fully decomposed eudialyte, several assemblages of secondary minerals are distinguished. Most assemblages are dominated by catapleiite as the main replacing Zr-phase (35 wt\% ZrO\(_2\)). Catapleiite compositions range from a nearly pure Na-end-member to being Ca-rich (up to 0.6 apfu Ca). Aegirine is the main Fe-bearing phase in nearly all pseudomorphs. Nacareniobsite-(Ce) is found in most assemblages and hosts most of the Nb and REE contents originally present in the eudialyte (Fig. 1b). Both aegirine and nacareniobsite-(Ce) have near-ideal end-member compositions. This is in contrast to their magmatic counterparts, which show significant solid-solution trends in the aegirine-augite\textsuperscript{17} and rinkite-mosandrite-nacareniobsite-(Ce) series\textsuperscript{18}.
Figure 1: Back-scatter electron (BSE) images of eudialyte and pseudomorphs after eudialyte; (A) Euhedral eudialyte crystal (Layer 4 Black) with 8-fold sector zoning, µm-scale oscillatory zoning and multiple concentric rims; (B) Common eudialyte pseudomorph assemblage (Layer 1 red), with catapleiite (Cat), interstitial albite (Ab), prismatic nacareniobsite-(Ce) (Ncr), acicular Ca-poor A1-silicate (A1, see text) and aegirine (Aeg). Pseudomorph surrounded by arfvedsonite (Arf) and exsolved feldspar (Ab and Ksp); (C) Part of pseudomorph (Layer 3 white) with monazite (Mnz), apatite (Ap), fluorite (Fl), catapleiite, aegirine and albite; (D) Part of pseudomorph (Layer 2 white) with unknown Ba-REE-Nb-phase (Brn), catapleiite, interstitial aegirine, analcime (Anl) and nacareniobsite-(Ce) between the catapleiite plates.

Analcime, albite and/or potassium feldspar are found in most assemblages, filling the interstitial space between catapleiite and other phases (Fig. 1b,c,d). Pectolite is also common and is often found intergrown with aegirine. Rare earth elements are concentrated into a wide range of minerals, many uncommon, and generally present as µm-sized crystals. The most commonly observed mineral is a Ca-rich or Ca-poor REE-silicate containing up to 65% TREO. These REE-minerals were first described by Karup-Møller et al. (2010), as new REE-phases with a presumed apatite structure.
(possibly P-poor members of the britholite-group) and were referred to as Ca-rich and Ca-poor A1, respectively. The REE-minerals occur as clusters of acicular crystals randomly distributed in the pseudomorphs (Fig. 1b). More P-rich varieties, approaching compositions of britholite-(Ce) (following a $\text{REE}^{3+} + \text{Si}^{4+} \leftrightarrow \text{Ca}^{2+} + \text{P}^{5+}$ coupled substitution scheme), are also present in several decomposition assemblages. A Ba-REE silicate (8 wt% BaO, 2% $\text{Nb}_2\text{O}_5$, 55% REO (La+Ce+Nd) and 22% $\text{SiO}_2$) is found in six samples. The mineral is texturally indistinguishable from the more common REE-silicates described above and forms similar aggregates of acicular crystals (Fig. 1d). Several REE-phases typically occur together in a single pseudomorph. At higher P contents, pseudomorphs contain monazite as the main REE-bearing phase, associated with secondary apatite and fluorite. Monazite-bearing assemblages have only been observed in two samples of the present study, both in white kakortokites (Fig. 1c). Because magmatic eudialyte contains virtually no P and only ppm-level F and Ba, these components are presumably introduced by the alteration-mediating fluids. The absence of Cl-bearing phases in the pseudomorphic assemblage suggests a significant net loss in Cl from these domains, which is consistent with the findings of Karup-Møller et al. (2010). Niobium mainly partitions into nacareniobsite-(Ce), although some pseudomorphs contain additional Nb-phases, i.e. pyrochlore, fersmite or fergusonite as small (<5μm) dispersed grains$^{7,8,14}$. The alteration of eudialyte is associated with zeolitisation (primarily analcime) of feldspars and feldspathoids and replacement of magmatic arvedsonite by secondary aegirine along the margins of the pseudomorphosed eudialyte grains (Fig. 1b).

**Extent of alteration**

The alteration of eudialyte ranges from partial replacement along the margin and cracks of EGM crystal to complete pseudomorphic replacement. In hand specimen, altered EGM are easily recognised by their pale orange-grey colour, which is distinctly different from the glassy pink original eudialyte. Eudialyte pseudomorphs cluster in zones of intense alteration, but completely decomposed grains may equally be in direct contact with fully preserved crystals. No petrographic link is observed between the distribution of the pseudomorphically replaced eudialyte and the proximity to cracks or veins that could have provided a pathway for percolating fluids. It is therefore suggested that the alteration occurred as a result of reactions with late-stage magmatic fluids present at crystal boundaries and in interstitial spaces at the final stages of solidification. The varying assemblages (monazite vs REE-silicate A1) could reflect variations in the composition of the evolving interstitial magmatic fluids, which may be linked to the local mineralogy e.g. the presence of magmatic apatite, fluorite or sodalite. The extent of eudialyte alteration is independent of lithology and is extremely variable throughout the kakortokites, complicating precise evaluation of the degree and mode of alteration and net loss or gain of elements. Current observations
suggest that up to 20% of the primary eudialyte is altered, i.e., 20% or more of the REE, Nb and Zr potential is contained in minerals not currently targeted for processing.

Discussion
Extensive auto-metasomatism and pseudomophic replacement of primary magmatic minerals due to a continuous transition from melt to hydrothermal fluid in the final stages of solidification is a common feature of agpaitic complexes\textsuperscript{19}. Late magmatic fluids are dominated by H\textsubscript{2}O-CO\textsubscript{2} or CH\textsubscript{4} and generally enriched in Na, Cl and F, allowing them to complexate and remobilise HFSE and REE\textsuperscript{19,20}. Remobilisation of incompatible elements by such fluids can both up and down-grade the resource potential, and is hence an important aspect in the paragenesis of alkaline rocks.
This study clearly demonstrates the wide-spread decomposition of eudialyte into complex aggregates of secondary minerals. These aggregates are invariably dominated by catapleiite-group minerals, suggesting alteration by Na-rich, hydrous fluids. Zircon-bearing assemblages have not been described from the current sample set and are apparently only related to severely altered kakortokites and pegmatitic rock types within the complex\textsuperscript{7,8}.
Late-stage alteration of eudialyte has also been described from North Qoroq, Greenland\textsuperscript{15}; Pilanesberg, South Africa\textsuperscript{14} and Sushina, India\textsuperscript{21}, indicating a large variety in possible eudialyte replacement products depending on both the primary composition of the eudialyte and the physico-chemical parameters of the metasomatising fluids. An overview of reported eudialyte decomposition assemblages is provided by Mitchell and Chakrabarty (2012). In all cases, the bulk compositions of the replacing phases reflect the initial composition of the primary eudialyte, and distinct fractionation of the HFSE and REE into the secondary phases is observed. In the case for Kringlerne, we infer that the auto-metasomatic alteration of eudialyte is not associated with large-scale remobilisation of the elements of interest and does not affect the overall ore grade of the deposit. Irrespective, the increased complexity of the secondary REE-, Nb, and Zr- paragenesis and major reduction in grain size (< 10 \(\mu\)m) will have a significant impact on the recovery of the ore metals.
An important step in optimizing ore recovery is to include the secondary REE, Nb and Zr assemblages in the magnetic separation process. It is currently unknown how the alteration products of eudialyte are distributed during magnetic separation and whether they are concentrated in the eudialyte separate (i.e. the REE-Nb-Zr ore) or the other separates. Two aspects are thus worth considering in future processing tests of eudialyte concentrates: 1) the magnetic susceptibility of the secondary ore minerals and 2) the dissolution kinetics of the secondary phases in relation to the acid treatment procedures used for eudialyte. An example provided by Zakharov et al. (2011) indicated that low Zr recovery from Lovozero eudialyte concentrates was related to the presence of acid resistant Na-Zr-phases, which formed as a consequence of late-stage magmatic alteration of eudialyte. Similar complications may be expected for Zr,
REE and Nb recovery from Ilímaussaq eudialyte concentrates with secondary phases that are insoluble during eudialyte dissolution procedures. Subsequently, acid treatment should be optimised for digestion of secondary ore bearing phases in addition to eudialyte.

Conclusions
The kakortokites at the Ilímaussaq Intrusion provide a world-class REE, Zr and Nb deposit which is unique in its size, exposure and mineralogy. Partial decomposition of the primary ore mineral eudialyte through interaction with late-stage magmatic fluids formed complex secondary REE-, Nb- and Zr- phases, such as catapleiite, nacareniobsite-(Ce), britholite-(Ce), monazite and fergusonite-(Ce). The alteration led to increased dissemination and fractionation of the prospective metals in the host rock, while leaving the overall ore grade intact. Further studies on the mineralogical properties and extraction techniques of the secondary REE-, Nb- and Zr- minerals will be of great value for optimal beneficiation of the kakortokites, with potential applications to other agpaitic ore deposits.

References


REE- MINERALS IN CARBONATITE, ALKALINE AND HYDROTHERMAL ROCKS, NORTHERN AND CENTRAL FINLAND

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Abstract

REE-rich minerals were identified and analyzed by electron microprobe from different targets located in the northern and central Finland. Both primary and hydrothermal minerals were found namely: phosphates (monazite-Ce), fluor-carbonates (bastnaesite-Ce), hydrated carbonates (ancylite-Ce), hydrated aluminium silicates, (allanite), oxides (fergusonite) and U-Pb rich minerals. Sokli Jammi- Kaulus carbonatite veins are enriched in LREE, P, F, Sr and Ba hosting in ancyline, bastnaesite, apatite and monazite. Allanite-(Ce) and fergusonite (Y) are abundant in alkaline gneiss of the Katajakangas REE-occurrence. The Korsnäs Pb-REE deposit includes apatite with monazite inclusions, calcio-ancylite and bastnasite. The Määrä- Vaulo REE-prospect in arkosic gneisses is dominated by monazite, allanite and xenotime. Albitites at Enontekiö contain bastnasite, monazite, allanite, xenotime and U-rich minerals include davidite, masuyite and sayrite. The Honkilehto Au-Co-S-mineralization at Kuusamo is characterized by U-rich minerals with bastnasite and allanite. The results obtained provide vital insights into the mineralizing processes associated with REE-prospects in northern and central Finland.

Introduction

Economic REE deposits are not known in Finland. However, REEs were extracted in the 1960’s century as a by-product in the fertilizer production from the apatite concentrates of the Kola Peninsula and the Korsnäs Pb mine in western Finland (1). In addition, small Nb- REE deposit, related with alkaline gneissic granite, from Otanmäki, Central Finland has been reported (2). During 2009-2012, the REE potential of Finland was studied by Geological Survey of Finland and potential source areas were identified according to the existing data and preliminary field studies (Fig. 1). The Fennoscanadian Shield hosts several P-REE deposits in the Devonian Kola alkaline province in NW Russia.
and Finland (3, 4). The Sokli carbonatite complex (total area 20 km2) is part of the province (5, 6) and recent geochemical studies have confirmed that the area hosts high REE potential. This study has been focused on the fenite aureole and associated late-stage cross-cutting carbonatite dykes that seem to have the highest potential for REE mineralisation in the Sokli area (7). The REE-rich accessory minerals bastnaesite, monazite, allanite, fergusonite and xenotime play a key role in the storage and mobility of geochemically important trace elements (LREE, Y Th and U) and are relatively common accessory minerals in carbonatite veins and fenites.

Figure 1: Location map of the studied areas.
In this study, backscattered electron (BSE) imaging and electron microscope analysis (EDS) are used to document various mineralogical characteristics and paragenesis of various types of REE minerals from different localities in Finland. The principal REE-minerals in studied rocks are phosphates (monazite-Ce), carbonates (bastnaesite-Ce), hydrated carbonates (ancylite-Ce), hydrate aluminum silicates (allanite), and oxides (fergusonite). Other REEs such as britholite, thorite, carbocernaite and columbite have been reported from some of the studied samples.

The research was circled around three objectives: (1) to study the REE, Y, Th and U composition of the major minerals; (2) to learn the nature, abundance, composition, grain-size distribution, textural relationships and associations of REE, Y, Th, U-rich accessories; (3) to determine the relative contributions of accessory minerals to REE, Y, Th and U.

Samples and analytic methods

The samples were collected from drill cores and outcrops of 6 different targets (Table 1). More than 50 polished thin sections were prepared from representative specimens of REE-mineral assemblages and examined under a polarizing microscope. The mineral compositions were analyzed by scanning electron microscope (SEM) JEOL JSM 5900 LV, at the Research laboratory of the Geological Survey of Finland (GTK), Espoo. Mineral chemistry was investigated by standard electron microprobe techniques on polished sections, using CAMECASX100/LKP at the Research laboratory, GTK, Espoo. The accelerating voltage was 15keV with beam current of 20nA. In order to detect fluorine in the analysis, spot size was kept 5 μm, whereas 1 μm was used where fluorine was not desirable.

Mineralogy and mineral chemistry

More than twenty REE-bearing minerals have been identified in the studied samples from different target areas in Central and North Finland. The mineralogy and paragenesis of accessory REE-rich minerals and the associated minerals are summarized in Table (1). Representative EPMA analyses of the REE-bearing minerals are presented in Table (2). It is obvious Ce predominates over both La and all other REE in most of the studied samples.

Jammi and Kaulus carbonatite veins in Sokli complex
The Sokli carbonatite (ca. 360-380 Ma) in northeastern Finland is part of the Kola alkaline province and hosts an unexploited phosphate deposit enriched in Nb, Ta, Zr, REE and U (4,8). The carbonatite intrusion consists of a magmatic carbonatite core, which is surrounded by a metacarbonatite and a wide fenite aureole, altogether about 9 km in diameter. The late-stage carbonatite vein dykes in the central fracture zone and in the fenite zone have a high potential for REE mineralisation (8, 9). The REE minerals that occur in Jammi and Kaulus carbonatite veins are almost entirely LREE ancylite-(Ce), calcioancylite-(Ce), monazite, allanite and bastnaesite (Ce). Ancylite-(Ce) is the most common in carbonatite veins and occurs as coarse grained phenocrysts with an average diameter of 300 μm. Calcioancylite (Ce) is commonly associated with barite, strontianite and pyrite (Fig. 2a).

**Table 1: The main REE-minerals in studied samples.**

<table>
<thead>
<tr>
<th>Locality</th>
<th>Rock type</th>
<th>REE-mineral phases</th>
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<tbody>
<tr>
<td>Sokli Jammi and Kaulus</td>
<td>Carbonatite veins</td>
<td>F-apatite, Sr-apatite, monazite, bastnaesite, ancylite, strontianite, baryte</td>
</tr>
<tr>
<td>Katajakangas</td>
<td>Alkaline-gneiss</td>
<td>Allanite, monazite, ancylite, bastnàsite, parasite, fergusonite, euxinite columbite-tantalite and pyrochlore</td>
</tr>
<tr>
<td>Korsnäss</td>
<td>Carbonatite</td>
<td>Apatite, monazite, carbocernaite, calcio-ancylite, bastnaesite, and barytocalcite.</td>
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<tr>
<td>Mäkärä</td>
<td>Arkosic gneiss</td>
<td>Monazite, allanite and xenotime</td>
</tr>
<tr>
<td>Enontekiö Palkiskuru</td>
<td>Albite-carbonate rock</td>
<td>Bastnaesite, monazite, allanite, xenotime, davidite, masuyite and/or sayrite.</td>
</tr>
<tr>
<td>Honkilehto</td>
<td>Carbonatitemica schist</td>
<td>Bastnaesite, allanite, davidite, U-Pb minerals, U-Si minerals</td>
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</tbody>
</table>

Monazite (Ce) occurs most commonly in the form of microcrystalline, sporadic, isolated equidimensional crystals and associated mainly with apatite. The crystal habit of bastnaesite and allanite in the studied carbonatites appears to be acicular or needle-shaped forming either in radial accumulations or intricate cross-cutting grids within a variety of minerals such as albite and dolomite(Fig.2b). Apatite in late carbonatite veins contains significant amounts of REE2O3, which indicates that the rare earth elements could be a by-product in the future phosphate production at Sokli.

**Katajakangas**

The Katajakangas Nb-REE deposit is located within alkaline gneissic granite at Otanmäki, central Finland. The Nb-REE mineralisation consists of a few metres wide, narrow lenses or layers in sheared quartz-feldspar gneiss with riebeckite and alkaline
pyroxene. These narrow mineralised zones contain high concentrations of Nb, Zr, Y, Th and lanthanides, with an estimated Nb-YREE resource of 0.46 Mt with 2.4% RE2O3, 0.31% Y2O3 and 0.76% Nb2O5. The Zr and Th contents in the occurrence range from 0.7% to 1.5% and 0.1% to 0.2%, respectively (10). Drill core samples have relatively high HREE contents compared with samples from carbonatites (7).

New mineralogical data, which is obtained in this study, indicate that REE are present in allanite, monazite, anclylite (Ce), bastnäsite (Ce), parasite (Ce), whereas, Y is present in, fergusononite (Y), euxenite (Y) and yttroclumbite. Nb is present in columbite and fergusononite, whereas, U-Th occurs in uranpyrochlore (betafite) and in yttrolite (Y, TH).

Electron microprobe (EMPA) data indicates that fergusononite-(Y) host Nb and forms irregular grains that vary in size from 100µm to more than 400 µm. Fergusonite is not chemically homogeneous, many crystals display growth zoning with bright domains, (Fig. 2c). The bright domains show 2.5% U and high contents of Y (23%) and Nb (38%) as fergusononite (Y) mineral phase (Table 2). Allanite occurs as subhedral to anhedral crystals and exhibits oscillatory zoning (Fig. 2c). Zoning profiles of allanite (Ce) show increase in Ce2O3, La2O3 and Nd2O3, whereas decrease in CaO, FeO and Al2O3 from core to rim (Table 2). Allanite crystals also show acicular crystals and aggregates of radiating individual crystals (Fig. 2d).

**Korsnäs Pb-REE deposit**

The area is dominated by metasedimentary rocks such as mica gneiss calc-silicate gneiss and marble, which are recently interpreted as magmatic carbonatite, composing of coarse grained calcite, feldspar, diopside, REE-bearing apatite, monazite, barite, britholite and anclylite. Two groups of sample from the Korsnäs are represented. The first group is calcite-marble or carbonatite characterized by enrichment in volatile-bearing REE-carbonates, anclylite-(Ce) and bastnäsite-(Ce), with traces of monazite. Analyses of multigrain calcio-ancylite grains are rich in LREE as Ce (~45%), La (~25%) and Nd (~12%). whereas bastnäsite contains 21–75 wt% REE2O3, 1.3–7.5 F and 20–77% CaO.

Back-scattered electron (BSE) imaging of multiple grains of calcio-ancylite revealed the presence of Ca-ancylit grains disseminated through calcite (Fig. 3a). Ancylite varies considerably in form. Most crystals are subhedral, some are euhedral and in few cases form fine aggregates along bastnaesite. The second group of samples marked by abundant crystals of apatite with exsolution-induced domains of monazite grains, and the monazite contains 49 wt% REE2O3, P2O5 28 wt% and CaO 16 wt%. Back-scattered electron (BSE) imaging of studied samples show that monazite and britholite inclusions occur both randomly and in large clusters of monazite grains included within apatite grains (Fig. 3b).
**Table 2:** Electron microprobe analyses of REE-rich minerals from studied areas.

<table>
<thead>
<tr>
<th>Mineral chemistry</th>
<th>Allanite Katajakan gas</th>
<th>Ancylite Kaulus</th>
<th>Bastnäsite Mäkärä</th>
<th>Cerite Tan Belt</th>
<th>Davidite Enonte kö</th>
<th>Euxenite Honkile hto</th>
<th>Fergusonite Katajakan gas</th>
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Figure 2: BSE images of REE-bearing and associated minerals in studied rocks (a) Clusters of barite, strontianite (white) and ancyllite(grey) within calcite, (b) acicular crystals growth of bastnaesite within apatite and Sr-calcite, (c) irregular fergusonite (Y) grains, the bright core marks enrichment of U and/or Th, (d) acicular crystals of allanite within dolomite.

Mäkärä-Vaulo

Selection of the Mäkärä and Vaulo areas as REE-Au-target in the Tana Belt was based on LREE- and HREE-anomalies in regional till and bedrock geochemistry and Au intersections in previous drill holes. Earlier studies indicate that the hydrothermal quartz-haematite-pyrite veins in Mäkärä are generally narrow (1 mm - 2 m) and formed as tensional fractures (11). The anomalous REE contents in the Tana belt can be explained by the occurrence of bastnaesite, cerite, allanite and fine xenotime grains in arkosic gneisses. The REE composition of the minerals is characterized by enrichment in Ce, La and to a lesser extent Nd. The total REE content decreases from 75 wt % in cerite (Ce), 60% in bastnaesite to 25 wt % in allanite.
SEM–BSE imaging of arkosic gneiss core samples from Mäkärä and Vaulo reveals that xenotime occurs as scattered grains within Ti-bearing minerals and as overgrowths on zircon. Allanite as the main REE-bearing mineral in the studied samples, occurs as spheroidal aggregates or as fillings vugs or cavities with albite, and the chlorite and bastnaesite replacing the allanite grains (Fig. 3c). Electron microprobe analyses EPMA along the opened fractures in some spheroidal aggregates, have shown needle-like bastnaesite crystals and fine apatite grains filling these spaces (Fig. 3d).

**Figure 3:** BSE images of REE-bearing and associated minerals in studied rocks. (a) Ca-ancylite grains disseminated through calcite, (b) discrete and coarse crystal of apatite with exsolution-induced domains of monazite clustering, (c) vug-filling texture; chlorite altered to allanite (in the rim) and later to bastnaesite in the center (light grey), (d) euhedral to subhedral bastnaesite grains filling the vugs and fractures within quartz.
**Enontekiö**

The Enontekiö area is characterised by variable rock types; albitites, syenite and carbonatite veins. In this study four samples were selected for chemical and mineralogical analyses. The carbonatite vein sampled contains 2.8% P₂O₅, 0.45% REE and 256 ppm Nb and characterized by high content of REE minerals as allanite, ancyllite, bastnaesite and xenotime. The albitites samples characterized by high content of U-Pb minerals such as davidite- (Ce), mausuyite and sayrite as well as high content of apatite, allanite and monazite. The allanite presents as fine-grained aggregates associated with monazite, apatite and zircon and exhibits a well-developed chemical zoning with Fe- and REE poor core and an Fe- and REE-rich margin. Despite the good abundance of allanite in the Enontekiö samples (<1%) it represents an important mineral phase in this locality since it contains more than 40% LREE (Ce, La, Nd). Monazite is, after allanite, the most important LREE carrier in albitites rocks of Enontekiö, where it appears as isolated minute crystals with a diameter usually smaller than 50—60 µm. Multigrain analyses show that the monazite-(Ce) is rich in LREE as Ce (~38%), La (~20%), Nd (~10%), CaO (1.5%), P₂O₅ (28%) and F (<1%). Bastnäsite is found in most studied samples of Enontekiö rocks, it crystallised around davidite or occurs as vein filling (Fig). EPMA analysis of bastnasite grains indicate that F more than 3%, and the predominance of LREE (> 65%), with Ce₂O₃ (35-37%), La₂O₃ (14-17%) and Nd₂O₃ (11.5-13.5%). Davidite as most common U-Pb minerals in Enontekiö area occurs in association with bastnaesite and allanite. Davidite is zoned, as shown by bastnaesite inclusions found near the rim of one grain, and a darker central region in the same grain (Fig. 4a). Reconnaissance EPMA traverses show that this zoning, at least in part, reflects the uneven distribution of elements Fe, Y, Si and U. Uranium, Cr, Ti and Pb tend to be relatively concentrated toward the central (more altered) portion of grains at the expense of Pb. Darker areas thus have maximum U, Pb and minimum Ti (Fig. 4b).

**Honkilehto**

The Kuusamo Schist Belt is an Au-Co-Cu-U occurrence with no resource estimate available. It is mainly hosted by albitised, biotitised and sulphidised sericate quartzite (12, 13). The studied samples characterized by occurrences of REE-minerals (bastnaesite, allanite) and U-Pb (davidite) with high content of Cr-magnetite and apatite.

Bastnaesite crystals are envelope-shaped around the U-Pb minerals or as isolated fine grains around the U-minerals (Fig. 4c). In Honkilehto, two phases of U-rich minerals recognized; firstly U-Pb rich minerals (richtetite) contain high uranium content 75% U, 20 Pb and 5% Y, Fe , secondly the U-Si rich mineral (bijvoetite) contain less UO₂ (~65) with Si(~15%). Intergrowth of these two minerals exhibit cauliflower form in most
studied U-Pb and U-Si phases (Fig. 4d). All of these U-minerals are associated mostly with bastnaesite and allanite.

**Conclusions**

Detailed mineralogical characteristic revealed three distinct types of REE-mineralization as phosphates, carbonates and silicates in studied areas. Mineralogical and mineral chemical analysis demonstrate that hydrothermal processes were responsible for the REE mineralization in the studied rocks and confirms that such processes are predominant in the formation of REE minerals in carbonatites, calc-silicate rocks and albitites. During late-stage processes apatite and carbonate minerals have been replaced by various assemblages of REE-Sr-Ba minerals in carbonatites.

The results obtained provide a useful reference basis for possible future feasibility studies, as well as important mineralogical insights into the varied rock types and mineralizing processes associated with the occurrence of elevated REE in northern Finland.

![BSE images of REE-bearing and associated minerals in studied rocks.](image)

**Figure 3:** BSE images of REE-bearing and associated minerals in studied rocks. (a) Bastnaesite growth in the rim of davidite or filling vugs within albite, (b) zoning in
davidite grain related to the concentration of (Pb-U) versus Ti, (c, d) U-Pb minerals (bright) surrounded by bastnäsite (grey).

References

Rare-earth elements minerals in carbonatites of the Kola Alkaline Province (northern Fennoscandia)

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Abstract

Various rare earth elements minerals occur in late-stage carbonatites within the Kola Alkaline Province. The carbonatites are mineralogically diverse rocks and contain calcite, dolomite, magnesite, siderite and rhodochrosite as rock-forming minerals. REE-minerals are present as accessory, minor and rock-forming minerals related to two distinct mineral assemblages: primary (magmatic or crystallized from carbohydrothermal solution – e.g. burbankite) and secondary (metasomatic – e.g. ancylite). The REE-minerals tend to be enriched in light REE, with the Y-rich mckelveyite-group minerals as rare exceptions. Stable and radiogenic isotopes indicate a deep mantle source for C, O, Sr and Nd in primary minerals and it is thought that the original formation of REE rich carbonatites was a result of multi-stage fractional crystallization of silicate-carbonate melts.

Introduction

Rare earth-rich carbonatites are here defined as carbonatites containing levels of rare earth elements (REE) as oxides of 1 wt.% and higher in which REE minerals often attain rock-forming concentrations. In a recent review of compositional and mineralogical data for Kola carbonatites (including Khibina, Kovdor, Vuoriyarvi and Turiy Mys) (Zaitsev et al., 2014) established a threshold for the content of REE at 2,000–3,000 ppm, above which REE-minerals are likely to be present. Such rocks are potential economic sources of REE and although none of the examples cited in this paper have been mined for REE, several have previously been exploration targets.

Where successive generations of carbonatite can be defined, all varieties of REE-rich carbonatites are always observed to be late-stage rocks. Many occurrences are assumed to be products of crystallization from (carbo-)hydrothermal fluids (e.g. Fen, Norway; Seblyavr, Kola Alkaline Province) and often all REE-minerals in carbonatite are
grouped in this category. However, magmatic origins have been thought possible, and indeed likely for other occurrences (Mountain Pass, USA).

**Kola carbonatites**

The Kola Alkaline Province contains twenty two complexes (380-360 Ma) consisting of various ultrabasic and alkaline rocks, they are, in order of their formation: olivinites, clinopyroxenites, melilititic rocks (turjaites, uncomphagrites, okaites) and foidolites (melteigites, ijolites, urtites). Nepheline syenites (foyaites, khibinites, luyavrites) are principle rock types at two giant Khibina and Lovozero complexes (Fig. 1).

The carbonatites are the youngest intrusive phase in Kola ultrabasic-alkaline complexes and they form multi-stage complex intrusions containing several varieties of carbonatities. They are mineralogically diverse rocks and contain calcite, dolomite, ankerite, kutnahorite, magnesite, siderite and rhodochrosite as major rock-forming minerals. Other typical minerals are represented by forsterite, diopside, phlogopite, tetraferriphlogopite, magnesioarfvedsonite, richterite, apatite and magnetite (Wall & Zaitsev, 2004).

Calcite carbonatites are the early-stage carbonatites (in terminology of Kapustin (1980)) in Khibina, Vuoriyarvi, Seblyavr and Sallanlatvi, while late-stage carbonatites are quite different in terms of mineralogy in these localities. Dolomite, and rarely ankerite carbonatites are known from Vuoriyarvi, Seblyavr and Sallanlatvi, magnesite and siderite carbonatites are present at Sallanlatvi, and Mn-rich carbonatites (including kutnahorite and rhodochrosite varieties) occur at Khibina.

The Kola carbonatites are characterised by the diverse mineralogy of their accessory minerals, and some of these can attain major or minor minerals status in late-stage rocks. They contain assemblages of various primary and subsolidus minerals of REE (e.g. burbankite and carbocernaite in Khibina and Vuoriyarvi, cordylite and kukharenkoite in Khibina and ancylite in all carbonatites) and Nb and Zr (e.g. pyrochlore, uranpyrochlore and bariopyrochlore at Khibina; lueshite and pyrochlore at Sallanlatvi).

The REE-mineralisation in the Kola carbonatites is highly variable ranging from tens of ppm in REE-poor Turiy Mys carbonatites to several wt.% in REE-rich Khibina, Vuoriyarvi and Sallanlatvi carbonatites. All carbonatites are enriched in light REE compared with heavy REE with (La/Lu)$_{CN}$ ratio between 9.3 and 1230 (Zaitsev et al., 2014).
REE-minerals

A total of twenty-five REE-minerals are known from the Kola carbonatites (Wall & Zaitsev, 2004). Mostly, they are carbonates, including unhydrous sodium-rich burbankite and carbocernaite, hydrous ancylite, Ca- and Ba-fluocarbonates synchysite, bastnäsite and cordylite; in addition to oxides (loparite), silicates (cerite) and phosphates (monazite) (Table 1).

Burbankite is a typical early-crystallised mineral in Khibina and Vuoriyarvi late-sage carbonatites, of which the latter also contains calcio Burbankite. These minerals form crystals up to 7 cm long and 4 cm diameter, euhedral hexagonal crystals; also they occur as 10-250 μm drop-like inclusions hosted by calcite or dolomite-ankerite or mineralized along boundaries of calcite/dolomite. The minerals have low birefrigence and optical data resembling apatite. Burbankite and calcio burbankite contain up to 21.7 and 18.5 wt.% REE₂O₃ respectively in Khibina and Vuoriyarvi.

Burbankite and calcio burbankite often show variable degrees of alteration and several assemblages of secondary minerals have been established. Rather simple assemblages, ancylite+strontianite+baryte and synchysite+strontianite+baryte, are typical for the Khibina carbonatites but the pseudomorphs after burbankite-carbocernaite in Vuoriyarvi are very complex with carbocernaite, ancylite, alstonite, olekmenskite, baryte, monazite and Sr-enriched calcite (Fig. 1).

Neither burbankite nor calcio burbankite have been found in the Seblyavr and Sallanlatvi carbonatites but a few samples contain “pseudomorph-like” polycrystalline assemblages of ancylite, strontianite and baryte that suggest the possible former presence of burbankite.

Ancylite is another common REE mineral for the Kola carbonatites. Typically it forms veinlets and thin veins within burbankite-calcio burbankite, and also full pseudomorphs (with strontianite and other minerals) after these minerals. Also, ancylite forms monomineralic veins cross-cutting carbonatites and occurs as euhedral crystals in rock cavities, containing up to 46.5 wt.% REE₂O₃.

Examples of rare REE minerals are the Ba fluocarbonates (cordylite and kukharenkoite) in Khibina carbonatites and Y-rich hydrous carbonates (mckelveyite, donnayite and ewaldite) in Khibina and Vuoriyarvi carbonatites. These minerals are the latest in the crystallisation sequence of the rare earth minerals. While cordylite and kukharenkoite
are well studied minerals, the mckelveyite group minerals are not well characterised, particularly their crystal structure.

**Origin of REE carbonatites**

Studies of Kola REE-rich carbonatites (Wall & Zaitsev, 2004) have shown that there are two groups of rare earth minerals. The first consists of primary minerals crystallised directly from a magma or carbohydrothermal solution; examples are burbankite, calcioburbankite, synchysite, bastnäsite (magmatic minerals), ancyline, mckelveyite (hydrothermal minerals). The second group consists of secondary minerals that were formed during replacement of early-formed REE minerals; ancyline and synchysite are the best examples of these.

Stable and radiogenic isotopes for REE minerals from the Khibina and Vuoriyarvi carbonatites indicate a deep mantle source for C, O, Sr and Nd in primary minerals, but show significant changes for stable isotopes and no changes for radiogenic isotopes in secondary minerals (Zaitsev et al., 2002). Formation of REE rich carbonatites was probably a result of multi-stage fractional crystallization of silicate-carbonate melts (Chakhmouradian & Zaitsev, 2012).

![Simplified map of the Kola province showing the distribution of ultrabasic-alkaline-carbonatite complexes, kimberlites, lamproites and lamprophyres (after Bell & Rukhlov, 2004 in Wall & Zaitsev, 2004).](image)

**Figure 1**: Simplified map of the Kola province showing the distribution of ultrabasic-alkaline-carbonatite complexes, kimberlites, lamproites and lamprophyres (after Bell & Rukhlov, 2004 in Wall & Zaitsev, 2004).
Figure 2: Backscattered electron image showing relic of burbankite in platy crystal of synchysite (centre of image), strontianite (gray) and baryte (white).

Table 1: REE minerals in Kola carbonatites

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MINERALOGY AND GEOCHEMISTRY OF STRATEGIC METALS AND REE IN COASTAL HEAVY MINERAL SANDS FROM NISYROS VOLCANO, GREECE

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Abstract

The northern coast of Nisyros volcano, belonging to the Hellenic Volcanic Arc (HVA), hosts black sands with heavy minerals, which are herein investigated for the first time in the literature. This also the first study concerning heavy sands from the entire HVA. UCC-normalized bulk spidergrams indicated that the sands are enriched in V, HFSE (Nb, Ta, Zr, Hf), Co, Sn and P, while they are depleted in LILE and particular incompatible elements. The study by powder-XRD and SEM-EDS showed abundant feldspars, apatite, Fe-spinels, tourmaline, pyroxenes (with apatite inclusions), and ilmenite (with apatite and sulfide inclusions) together with zircons. The heavy mineral sands are also relatively enriched in REE (exhibiting a remarkable Eu negative anomaly) but the total content can be considered interestingly low (ΣREE+Y = 240 ppm). The studied volcanic weathered material was also compared to “fresh” volcanic material, that is a clayey material (alunite, anhydrite,opal-CT, quartz, kaolinite) currently deposited into Nisyros caldera main hydrothermal crater. This is enriched in volatile components (L.O.I. 33.7 wt.% compared to 1.4 wt.% of sands), S (14.28 wt.% compared to 0.10 wt.% of sands) and other chalcophile elements (Se, Bi, Hg, As, Pb), as well as in P and Ba. Thus, P is an element enriched in both weathered and “fresh” Nisyros volcanic materials, whereas there is a great contrast in Fe, Ti, HFSE and chalcophile elements. Moreover, the sands show different geochemical patterns compared to the volcanic rocks of the island which are particularly enriched in LILE. It is concluded that the weathering contributed to coastal accumulation of specific heavy minerals and strategic metals, including V (1920 ppm) and Nb (245 ppm), which are low compared to coastal heavy mineral sands of Greece and the globe. The same geochemical trends stand when comparing Nisyros sands with various volcanic rocks from the whole HVA.
**Key words:** Heavy minerals; strategic metals; rare earths; coastal sands; volcano; Nisyros

**Introduction**

The growing demand of strategic metals (e.g. Nb, Ta), actinides (U, Th) and lanthanides (REE) from the markets enhances geological exploration projects in order to find commodities which exhibit high exploitation and metallurgical extraction potential. Although the geological sources of the above elements exhibit a great variety, many studies have focused on placer deposits. Beach sands are mineral accumulations typically formed through weathering and erosion of either igneous or metamorphic rocks. Significant interest for further study show natural high magnetic black sands which are enriched in so-called heavy minerals. Their crystals are sufficiently resistant to weathering processes and their accumulation in coastal areas owns to the gravity segregation. The phases occurring in heavy mineral sands, in mixture with common tectosilicates and phyllosilicates, are Fe- & Cr-spinels, Ti-oxide minerals, phosphate minerals (apatite, monazite, xenotime, rhabdophane), and specific heavy silicate minerals such as zircon and allanite (epidote group). The above natural materials are rich, by nature, in strategic metals, actinides, and lanthanides. Heavy mineral sand formations are mainly found in ancient or modern ocean and sea beaches and occasionally within continental land masses \(^1\)\(^-\)\(^3\). However, sands commonly found in coasts of volcanic islands also show an economic importance, depending on the extraction ability of metals hosted in the crystal lattice of “accessory minerals” such as rutile, zircon and ilmenite \(^4\), \(^1\), \(^5\). On the other hand, heavy mineral sands show an increasing environmental importance due to the presence of actinides (U, Th, and their decay products) that could pose a radiological risk \(^6\), \(^7\).

Previous studies in Greece, concerned heavy mineral sands derived from plutonic rocks (i.e. granites), particularly in the long coast (240 km) west of Kavala city, in Touzla Cape near Thessaloniki city, and also in Sithonia peninsula coasts in Chalkidiki \(^8\)-\(^12\). In the frame of the present study we present, for the first time in the literature, mineralogical and geochemical data for coastal heavy mineral sands occurring in southern Greece, and particularly in Nisyros Island which is located in the Hellenic Volcanic Arc (HVA) at eastern Mediterranean Sea. More specifically we demonstrate the strategic metal (HFSE elements), REE and actinide elements potential of these sands. The coasts of the Mediterranean Sea are rich in heavy mineral sands of volcanic origin due to several volcanoes still active nowadays \(^13\). Thus, this paper could be
considered as a model study for sands from the whole HVA and from relevant volcanic areas in Mediterranean coasts.

Geology settings

The Hellenic Volcanic Arc (HVA) is a young 5 Ma-to-present volcanic arc that has developed in the pre-Alpine to Quaternary continental crust of the Hellenic Subduction System (HSS). Its development is related to the northward subduction of the last remnant of the oceanic crust of the African plate beneath the southern edge of the active margin of the European plate, resulting in the formation of numerous Plio-Quaternary volcanic centers, namely Crommyonia (Soussaki), Methana-Aegina-Poros, Milos-Komolos-Polyegos, Santorini (Thira)-Kolumbo and Nisyros-Yali-Kos. Nisyros volcano is composed of Quaternary volcanic rocks with alternating lava flows, pyroclastic layers and lava domes erupted during successive periods of activity. The evolution of this volcano is associated to a formation of a big caldera in the middle of the island, with significant post-volcanic activity. In fact, Nisyros constitutes a stratovolcano which has an average diameter of 8 km (based on sealevel niveau) with a caldera (4 km in diameter) formed during the explosive eruption of a large pumice. The oldest age of the volcanic rocks is about 160 Ka and the most recent phreatic eruption took place in 1867 AD. The caldera floor consists of several hydrothermal craters, with the largest (Stefanos) having a a depth of 27 m and diameter of 330 m. Hydrothermal venting from the craters continues to this day with the last significant hydrothermal eruptions occurring in 1871-1888 AD. Present-day activity is documented by fumarolic degassing of mainly H$_2$S, CO$_2$, H$_2$O, H$_2$ and CH$_4$. The pre-caldera period is characterised by a succession of four lavas and four pyroclastic flows that formed the stratovolcano. This succession was followed by the rhyolites of Nikia in the southern part of Nisyros and by pumice deposits. Post-caldera magmatic activity has produced a series of rhyodacitic domes (Profitis Ilias Synthem) that fill the north-western section of the caldera floor, as well as the south-western flank of the island. Geothermal drillholes have been studied in order to give information about the basement beneath Nisyros. The boreholes showed intersected units of diorite, limestone, and marble. In addition skarns have been detected and are formed by contact metamorphism and hydrothermal alteration of the limestones. Carbonate-rich rock-types are also found as xenoliths in some pyroclastic deposits on the island.
The volcanic stratigraphy of Nisyros has been described by many authors 17, 24, 26, 27. The earliest magmatism at Nisyros is also related to submarine flows that deposited porphyritic pillow lavas of basaltic-andesite composition that crop out on the northwestern shore, as a result of active uplift of this section of the island 28, 29. There is evidence of erosion and reworking of these volcanic rocks, indicating exposure above sea level for part of the depositional history 30. It should be mentioned that the black heavy mineral sands, occurring in the northern coast of the Island, have never been investigated by the aforementioned authors.

Material and methods

The sand samples (NISBS) have been collected from the northern coast of Nisyros Island (Fig. 1). The material appears as fine grained and it is black in the colour due to the high content in Fe-spinels and other dark heavy minerals. Furthermore, another clayey sample (NISC) has been collected from the recent deposits of the interior of the main hydrothermal crater of the Nisyros volcano caldera (Fig. 1). The second sample was considered to be studied for comparison reasons, as “fresh” volcanic material, in contrast to the weathered (re-processed) volcanic coastal sands.

The bulk chemical composition, concerning major and trace elements, was determined by Inductively Coupled Plasma Optical Emission & Mass Spectrometry/ICP-OES &-MS (PerkinElmer Sciex Elan 9000) after LiBO2/LiB4O7 fusion and HNO3-digestion of 0.2 g of sample. Loss on ignition (LOI), as well as total C and S, were also measured using standard methods. The mineralogical characterization was performed by optical microscopy, powder X-ray Diffraction/XRD (Siemens D5005 – now Bruker AXS- diffractometer), and Scanning Electron Microscopy/SEM–EDS (Jeol JSM-5600 equipped with Oxford EDS) in both free sand grains and polished-sections. The fine clay (2 - 0.2 μm) and ultrafine (nano) clay (< 0.2 μm) fractions of the materials, separated using standard wet-chemical and centrifugation procedures31, were also investigated with regard to raw, glycolated and heated samples (550 °C).
**Figure 1:** Sampling areas concerning black sands (NISBS) in the northern coast of Nisyros Island (a,b) and clayey material (NISC) in the floor of the main hydrothermal crater of the caldera (c,d).

**Results and discussion**

The UCC-normalized spidergrams, based on bulk chemical analyses, indicated that the studied coastal heavy mineral sands from Nisyros volcano (NISBS) are enriched in V, High-Field Strength Elements (HFSE, i.e. Nb, Ta, Zr, Hf), Co, Sn and P, while they are depleted in Large Ion Lithophilic Elements (LILE) and particular incompatible elements (**Fig. 2 upper**). Thus, V concentration has been recorded to be 1920 ppm whereas Nb concentration 245 ppm. Moreover, concerning the REE content of the sands, chondrite-normalized patterns (**Fig. 2 lower**) showed that they are enriched mainly in LREE ($\Sigma$LREE = 193 ppm) rather than HREE ($\Sigma$HREE = 20 ppm), but the total content can be considered interestingly low ($\Sigma$REE+Y = 240 ppm) in respect to heavy mineral sands. Europium negative anomalies are characteristic in all REE patterns including those corresponding to various rocks of the HVA. Chondrite-normalized patterns in previous
study for Nisyros volcanic rocks showed LREE-enrichment, with similar slight negative Eu anomalies only apparent in the andesitic samples. Alternatively, the different degrees of LREE and HREE enrichments may be also be due to magma composition variations\textsuperscript{32}. On the other hand, the studied “fresh” volcanic material (NISC), currently deposited into Nisyros caldera main hydrothermal crater, is enriched in volatile components and other chalcophile elements (Se, Bi, Hg, As, Pb), as well as in P and Ba. According to the same spidergrams, the material is depleted in LILE as well. The REE content, compared to the volcanic weathered material (i.e. the sands), is remarkably lower (ΣREE+Y = 96 ppm), while Eu anomaly also shows a slightly different trend. Besides, the L.O.I. of NISC is extremely high (33.7 wt.% compared to 1.4 wt.% of sands) accompanied by a high S content (14.28 wt.% compared to 0.10 wt.% of sands). That implies abundant hydrated, hydroxylated, and sulfate mineral phases. It is therefore worthy to note that the heavy mineral sands show different geochemical patterns compared to the caldera material. Only P is an exception due to the fact that it is an element that occurs in elevated concentration in both weathered/re-processed and “fresh” Nisyros volcanic materials, whereas there is a significant contrast in Fe, Ti, HFSE and chalcophile elements.
**Figure 2:** UCC-normalized spidergrams (upper) and chondrite-normalized REE patterns (lower) for Nisyros black heavy mineral sands (NISBS) and hydrothermal crater material (NISC), compared to volcanic rocks from Nisyros and the entire HVA.

According to a Eu/Eu* - Ce/Ce* discrimination diagram, recently proposed for sedimentary geological materials\(^3\), the caldera crater “fresh” material is closer to the massive sulfides field, while the sands, along with the HVA rocks, are closer to the average volcanics (Fig 3 upper). Additionally, the sands seem to be part of sediments-partial field using a \((\text{Ce/Yb})_{\text{NASC}} - (\text{La/Sm})_{\text{NASC}}\) discrimination diagram (Fig. 3 lower), for the reason that the material is weathered and re-processed.
Figure 3: REE discrimination diagrams for sedimentary geological materials (Leybourne & Johannsen, 2008), as applied to NISBS, NISC, and rocks from Nisyros and the entire HVA.
Figure 4: SEM-EDS data indicating strategic metal-, REE- and actinide-bearing heavy minerals in the studied Nisyros sands.

The powder-XRD and SEM-EDS study of the sands showed common tectosilicates (feldspars and particularly plagioclase), together with abundant phosphates (apatite), Fe-spinels (magnetite, ulvospinel), tourmaline, clino- and orthopyroxenes (with apatite inclusions), and ilmenite (with apatite and sulfide inclusions) as well as zircons (Fig. 4). Tourmaline crystals appear as elongated trigonal prisms, with smaller, second order prism faces on their corners. Tourmaline had also been mentioned in rhyolite dykes, most likely Pliocene, from Ikaria Island in the Aegean
back-arc region\textsuperscript{34}. Pyrite and barite have also been identified in the sands. It is notable that micro-inclusions of sulfides, together with apatite needles, are occasionally included in ilmenite fragments. Sulfides and sulfates may be significant scavengers of various trace elements related to bulk geochemical anomalies. It should also be mentioned that the studied Nisyros heavy mineral sands are rather coarse, in microscale (Fig. 4), and they do not contain a measurable clay (fine clay and nanoclay) fraction.

On the other hand, the XRD patterns of the raw clayely material from the hydrothermal crater of the caldera, showed that the main minerals are alunite and anhydrite, in accordance to bulk chemical analyses indicated high L.O.I. and S, as well as opal-CT and quartz. Besides, careful SEM-EDS investigation revealed distinct barite microcrystals with a characteristic platy morphology. Additionally, the XRD of raw, glycolated, and heated (550 °C) clay fractions indicated a significant amount of alunite and kaolinite-group minerals\textsuperscript{31}. Concerning the caldera floor crater and the southern caldera wall, surface expressions of an active hydrothermal system include hydrothermal deposits, fumaroles, mud pools and boiling water pools\textsuperscript{35, 36}. The caldera model\textsuperscript{36} is consisted of a magmatic body, at unknown depth, which supplies heat and fluids to the hydrothermal system, a deep boiling aquifer (situated at more than 900 m below sea level) and finally a shallow reservoir at variable temperatures fed by a mixture of vapor separated by the deep aquifer and meteoric water. Thermal springs and fumaroles represent the surface manifestations of the deep hydrothermal system of Nisyros, which has been directly attained by the geothermal wells Nisyros 1 and Nisyros 2\textsuperscript{27}. Previous studies have been mentioned a decrease in sulfate content that could be a result of sulfate minerals precipitation or reduction to sulfide. Alunite which is abundant also in the clay faction of the material is an evidence of precipitation of sulfates while the presence of pyrite could represent an example of sulfide reduction. That aspect has been pointed out by several authors\textsuperscript{38, 39, 20}. Geothermal wells both situated at the northeastern periphery of the craters were investigated about the existed hydrothermal minerals considering the water-rock interaction\textsuperscript{40}. Thus, the propylitic zone extends from 950 to 1547 m and it is marked by abundance of well-crystallized epidote, adularia, albite, quartz, pyrite, chlorite, and sericite-muscovite. Less abundant minerals such as anhydrite, stilpnomelane, wairakite, garnet, tremolite, and pyroxene, also exist. Moreover, previous mineralogical investigations indicated in the caldera material minerals such as halotrichite, alunogen, voltaite, gypsum, sulfur, and tamarugite\textsuperscript{41}, besides to alunite, anhydrite,
opal-CT and quartz. The volatiles and chalcophile elements, which are enriched in the NISC material, may be mainly associated to alunite. The alunite supergroup minerals are defined as having the general formula \( \text{DG}_3(\text{TX}_4)_2\text{X'}_6 \), where D is normally a large, mono- to tetravalent, ion in 12-fold coordination (e.g. K, Na, Ca, Pb, REE) or partial vacancy, G is usually a trivalent cation and minor divalent cations (e.g. Fe, Al), T is a penta- & hexavalent cation and minor \( \text{Si}^{4+} \), and \( \text{X'/X} \) is O, (OH), minor F and possibly \( \text{H}_2\text{O} \). Thus, \( \text{TX}_4 \) are characteristic alunite anions, usually \( \text{SO}_4 \), \( \text{PO}_4 \), or even \( \text{AsO}_4 \). As a consequence, certain positive geochemical anomalies of the caldera material, may be related to elements hosted in alunite T sites (P, As, and perhaps Se), whereas other elements, such as Bi, Pb and Hg, might substitute in D sites.

The heavy mineral sands from Nisyros volcano represent a weathered and re-processed material which originates mainly from the Quaternary acidic volcanic rocks, lavas, pyroclastic layers and domes. Nisyros rocks belong to the calc-alkaline series and their composition ranges from basaltic andesites to rhyolites. According to previous studies the volcanic rocks of Nisyros exhibit important mineralogical similarities in relation to the other volcanic centres of the HVA (Milos, Santorini, Methana) and therefore all above are included in the calc-alkaline trend and range from basaltic andesite to silicic rhyolite. The minerals identified in the sands fit to the geological background of Nisyros, taking into account all previous studies regarding petrology of the Island’s volcanics. According to mineralogical investigation, euhedral to subhedral crystals of plagioclases (with characteristic zoning) are abundant in Nisyros rocks. Moreover, that is a mineral phase which often shows abrupt compositional changes reflecting significant changes in chemical potentials that are commonly attributed to magma mixing, ascent, and degassing. Clinopyroxene, which is also abundant in the sands, has been mentioned as a major mineral phase of basaltic andesitic and dacitic rocks. However, orthopyroxene with hypersthenic composition is additionally present in the sands. In contrast, olivine and hornblende, which are common as phenocrysts in the parent volcanic rocks (lower andesitic lava flows, pyroclasts, post-caldera domes and their enclaves, dacitic and rhyolitic volcanic rocks), are not present in the sands. This is evidence that the above mineral phases were most likely dissolved during prolonged erosion and weathering processes, resulted in formation of heavy mineral sands. Fe-spinels (magnetite) and ilmenite are commonly present as microphenocrysts in the parent rocks, although the post-caldera dacitic- rhyolitic domes lack ilmenite. The black sands contain high content of magnetite and ilmenite, which is not unusual due to the fact that they are rather resistant to weathering processes. Hydrothermal pyrite has also been reported as inclusion in Fe-Ti oxides.
Among the accessory mineral phases, apatite is ubiquitous and is generally included in plagioclase and pyroxene, whereas zircon is only found in the most evolved rocks\textsuperscript{44,25}.

The positive geochemical anomalies, derived from the UCC-normalized spidergrams with regard to V, HFSE (Nb, Ta, Zr, Hf), Co, Sn and P, are consistent to the mineralogical composition. The intense presence of ilmenite affects the elevated content of Nb and Ta due to the fact that this metallic mineral may host such high-valence elements in its structure. Ti-oxides are likely to be the most important reservoirs of Nb and Ta in the mantle\textsuperscript{45,46}, although, if titanite is present, it will strongly affect the Nb and Ta partitioning. Remarkably high Nb$_2$O$_5$ content (0.28 wt.\%) has been detected in the magnetic fractions of ilmenite from the beach placer deposit of Chavara, southwest India\textsuperscript{47}. The positive anomalies of tetravalent Zr and Hf are justified from the zircons inclusions, which are abundant as inclusions in the pyroxene and ilmenite crystals. According to the literature they are present in all geological units of the Nisyros and are most likely part of mineral assemblages in rhyodacites to rhyolites. The main difference of zircons concerns their concentrations in some trace elements, including Ti, Hf, U, Sc, and Nb. The typically higher Hf, U, Sc, and Nb contents reflect the slightly more evolved melt composition from which these zircons are crystallized\textsuperscript{48}. Also, the Fe-spinels could host in their lattice the observed elevated amounts of V and Co. Furthermore, the P anomaly is obviously associated to apatite, derived directly from the parent volcanic rocks. Apatite supergroup concerns phases with the general chemical formula $^{IX}M_{12}^{VI}M_{23}^{(IV(TO_4))_3}X$ (Z=2), where many cations could substitute in M1, M2, T, or X site. Thus, V, which is enriched in the studied samples, except its predominant presence into Fe-spinels, may also be present (in the form of $[V^{5+}O_4]^{3-}$) into the apatite structure\textsuperscript{49}. Additionally, Co, and also Sn, may be associated to sulfide mineral phases. Hydrothermal pyrite contains significant amounts of trace elements (e.g. As, Pb, Sb, Bi, Cu, Co, Ni, Zn, Au, Ag, Se, Te), which can be specifically incorporated into nanoparticles\textsuperscript{50}. Most of the nanoparticles are crystalline and are excluded from the pyrite matrix or precipitated from the hydrothermal solution. Significant recrystallization is taking place under the conditions of increasing temperature and therefore the migration of the trace metals via diffusion through the pyrite structure and melt formation have been observed by many researchers\textsuperscript{51,52}. Recent studies have shown that many of the trace elements originally thought to be present in the structure of pyrite, are actually present as micro-inclusions\textsuperscript{53,50} abundant in early forms of pyrite. Whereas Ni, Co, and Se are commonly present in the pyrite structure, As, Cu, Zn, Pb, Bi, Sb, Tl, Mo, Ag, Cd, Mn, Hg,
and Te may be either in the structure or as sulfide micro-inclusions, and Ti, V, U, Ba, Sn, W, and Cr, are in variably present within micro-inclusions of matrix material.

Trace-element variation patterns in previous studies for Nisyros volcanics feature the characteristic subduction-related signature of relative enrichment in LILE (i.e. K, Cs, Rb, Ba, Pb), U, Th and Sr, and depletion in Nb and Ti \(^{32}\). However, the studied heavy mineral sands are depleted in LILE, which clearly indicates that the above elements are preferentially dissolved and removed upon prolonged weathering processes. Kanafí Synthem which represents the oldest volcanic unit of Nisyros volcano showed increased incompatible element (e.g., Zr, Nb, Ba, Rb, Ce) concentrations with increasing SiO\(_2\) or decreasing MgO, as it has also been observed in previous geochemical studies of Nisyros rocks \(^{23, 25, 54, 55}\). Lower Pumice and Upper Pumice glasses of Nisyros are characterized as high-K rhyolites \(^{56}\) and their chemical trends indicate elevated values of incompatible element of primitive mantle. Besides, negative anomalies at Nb, Ta and also at Ba, Sr and Eu, are consistent with the arc setting of Nisyros and with feldspar fractionation, respectively \(^{57}\). Empirical and computational studies have demonstrated that partitioning of tri- tetra- and pentavalent cations in clinopyroxene increases with increasing alumina content, due to enhanced coupled substitution of highly-charged elements on M sites with tetrahedrally-coordinated Al \(^{58, 59}\). Consequently, clinopyroxene is also a mineral which should play a crucial role in the accumulation of trace elements in the studied sands.

It is very crucial to mention that previous studies concerning coastal heavy mineral sands from northern Greece showed elevated concentration of REE and natural actinide elements \(^{8-12}\). In the case of Nisyros sands the REE content is comparably very low, but, on the other hand, the HFSE contents are much higher. It is evident that the type of the igneous parent rocks affects the mineralogical and chemical composition. Thus, it is concluded that in both cases acidic to intermediate igneous rocks are involved (Kavala pluton, Monopigado granite, Sithonia granite, and Nisyros volcanics), but it seems that volcanic rocks provide with less REE+Y (and actinides) and more strategic metals (namely V, Nb, Ta and Co). This conclusion, beyond the scientific interest, could be especially useful for future exploration and exploitation projects in Greece and the entire Mediterranean and southern Europe.
Conclusions

Coastal heavy mineral black sands derived, by weathering, from acidic volcanic rocks of Nisyros island, located in the Hellenic Volcanic Arc / HVA (southern Greece, eastern Mediterranean), differ significantly to similar sands derived from relevant plutonic rocks occurring in northern Greece (Kavala, Thessaloniki, Chalkidiki). The mineral constituents of the studied sands are feldspars, apatite, Fe-spinels, tourmaline, pyroxenes (with apatite inclusions), and ilmenite (with apatite and sulfide inclusions) together with zircons. The Nisyros sands are enriched in specific strategic metals (e.g. V = 1920 ppm and Nb = 245 ppm) and exhibit unusually low REE content (ΣREE+Y = 240 ppm). This weathered/re-processed material is also different, in terms of mineralogy and geochemistry, to Nisyros and HVA volcanic rocks, as well as to “fresh” volcanic clayey material (alunite, anhydrite, opal-CT, quartz, kaolinite) currently deposited into Nisyros caldera main hydrothermal crater. The later one is enriched in volatile components and other chalcophile elements, whereas according to Eu/Eu* - Ce/Ce* discrimination diagram it is closer to the massive sulfides field. The present paper is the first, in the literature, study of heavy mineral sands from the entire HVA, and could contribute to future exploration and exploitation of coastal sands in Greece and the entire Mediterranean and southern Europe.

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Session VI-B: REE Ore formation
RARE EARTH ELEMENTS IN KARST-BAUXITES: A NOVEL UNTAPPED EUROPEAN RESOURCE?

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Abstract

Karst-bauxite deposits form as a result of the accumulation of residual clay minerals in depressions on a karst limestone surface, and their subsequent lateritic weathering. Rare earth elements (REE) become concentrated in the bauxite deposits due to crystallisation of authigenic REE-bearing minerals, accumulation of residual phases and the adsorption of ions on clays and other mineral surfaces. All the REE are concentrated in the red mud waste generated by alumina production from bauxite through the Bayer process. Red muds thus contain on average 900 ppm REE compared with typical values of <100 ppm to ~500 ppm REE in the bauxites. Extraction of REE from red mud has been shown to be feasible although it is challenging due to the heterogeneous spatial distribution of REE in the bauxites and the need for development of appropriate processing methods. With annual European production of bauxite estimated to be approximately 3.5 million tonnes per annum, resulting in approximately 140 000 tonnes of red mud, understanding the REE resource potential of bauxites is integral to the assessment of European REE resources.

Introduction

Research into the rare earth element (REE) content of bauxites has a long history, with authigenic rare earth minerals first identified in the San Giovanni Rotondo deposit in Italy1. Further research by Maksimović and Pantó2,3,4,5,6,7,8 in particular led to the discovery of authigenic REE in multiple deposits in the Balkans and Greece (for example at Marmara, Greece, Vlasenica, Bosnia and Herzegovina and Štitovo, Montenegro). Research into the potential of bauxites as a source of REE, Sc and Y has been undertaken by many researchers over the past forty years (e.g. 9,10,11,12,13,14,15). This paper reviews this previous work to consider the REE resource potential of bauxites in Europe.
Bauxite is formed from the intense lateritic weathering of residual clays, which accumulate in topographic lows on continental surfaces. The two main classes of bauxites are: 1) those that form on aluminosilicate lithologies; and 2) those that form on limestone, known as karst bauxites, and which are the focus of this paper. Bauxite is the primary source for aluminium (Al) production globally and is relatively common in Europe, with deposits known from the majority of Mediterranean countries and intermittent exploitation occurring over many decades (Figure 1).

![Map of southern Europe showing selected bauxite occurrences](image)

**Figure 1:** Map of southern Europe showing selected bauxite occurrences as mentioned in the text: Olmedo, Sardinia, Italy (1), San Giovanni Rotondo, Italy (2); Parnassos-Ghiona, Greece (3), Marmara, Greece (4); Vlasenica, Bosnia and Herzegovina (5); Štitovo pit, Nikšić, Montenegro (6); Grebnik, Kosovo (7); Nagyharsany, Transdanubian Central Range, Hungary (8).

Demand for REE is increasing, particularly for use in green energy technologies, e.g. wind turbines etc. As China currently dominates global production, there is increasing pressure to identify alternative European sources of these economically important metals. The growing demand for REE has recently been emphasised by numerous authors, and while recycling may contribute to meeting future demand, the separation of individual REE from recycled materials is very challenging with only 1 per cent of REE currently recycled from end-of-life products (and references therein). There are currently no mines producing REE in Europe and although this is likely to change in the future, an alternative, readily available, source of REE would be attractive.

Red muds produced from alumina processing represents a potentially important concentration of REE as it has been shown that all of the REE pass through the alumina extraction process into the waste, and the total REE values are enriched by a factor of two from the original bauxite ore. Currently red mud is viewed as waste as it does not have any other purpose, although there have been attempts to find alternative uses for the material (and references therein).
**Bauxite**

Karst bauxite deposits are formed by accumulation of residual clays, derived from the weathering of aluminosilicate minerals\(^2\), in depressions on carbonate palaeotopography. The contents of the depressions are bauxitised through deep lateritic weathering and desilicification of ferrilitic soils\(^3\). The conditions under which bauxitisation occurs are such that silica is incongruently dissolved from minerals such as feldspar and kaolin leaving an aluminium-rich residue\(^4\). Bardossy\(^1\) distinguishes several subtypes: Kazachstonian type, Timan type, Ariège type, Tula type and Mediterranean type. These classifications are based on the composition of the deposits and the mode of karstification.

![Figure 2: Schematic diagram showing the typical classic Mediterranean type karst bauxite (after Bardossy 1982\(^1\)).](image)

Mediterranean type karst bauxite deposits formed on both the European and Adriatic Mesozoic carbonate shelves in the Neotethys realm during the Mesozoic to Early Cenozoic\(^5\,\(^6\). Bauxitisation in this area occurred from the surface downwards leading to the ultimate loss of SiO\(_2\) and Fe\(_2\)O\(_3\) and accumulation of Al\(_2\)O\(_3\) with depth\(^3\). This paper focuses on Mediterranean type karst bauxite.

**Rare Earth Elements in Bauxite**

Where REE are available to the weathering system, they can be adsorbed onto the surfaces of clay residues that form the bauxite deposit and are then concentrated with depth by bauxitisation\(^7\,\(^8\). With more intense bauxitisation there is a correlation with depth between both increased REE content and decreased silica content. Meteoric water can preferentially leach away silica produced from the dissolution of feldspar and kaolinite leaving an Al-rich residue\(^9\). However, the process of REE concentration is dependent on multiple factors and is still poorly understood.
Authigenic rare earth element-bearing minerals

Where sufficient REE are available within the bauxite, bauxitisation has occurred in situ and where there has been no later transport or erosion of the deposit, authigenic REE-bearing minerals can form. REE are mobilised from the clay as waters percolate through the system during bauxitisation. As REE-bearing fluids descend through the deposit and reach the carbonate they become physically trapped allowing authigenic minerals to form where REE content is sufficiently high\(^ {27,28}\); the most common is hydroxybastnäsite-(Nd) \((\text{Nd(CO}_3\text{)(OH)})\)\(^ {14,30}\). In order for REE minerals to develop, the initial concentration of REE adsorbed onto the clay must be greater than about 1000 ppm\(^ {14}\). If the initial concentration does not reach this threshold REE minerals are unlikely to form. Increases in REE content of up to almost six-fold have been recorded as a result of bauxitisation (e.g. at Nikšić, Montenegro and Grebnik, Kosovo\(^ {31}\) (and references therein)). Where the bauxites have been disturbed during formation REE can be lost from the system, such as in the karst-bauxite deposits in the Transdanubian Central Range in Hungary\(^ {32}\). In Hungary reported REE concentrations vary greatly, ranging from ~81~10 000 ppm. This is due to the detrital nature of some REE host minerals such as monazites sourced from the Mecsec mountains in the case of the Nagyharsany deposit, rather than authigenic mineral growth \(^9\).

Conditions of mineral formation

Key parameters controlling the concentration of REE in bauxite include intensity of leaching by meteoric waters, pH, Fe content and the availability of ligands such as fluorine (F).

**Water flow:** Leaching of the bauxite by meteoric water can readily remobilise adsorbed REE\(^ {14}\). The weathered limestone below the bauxite facilitates drainage and thus clay layers do not form within the bauxite, so the downward mobility of REE is not restricted\(^ {33,26}\).

**pH:** The alkaline nature of the underlying limestone creates a high pH that results in increased stability of REE-carbonate complexes (e.g.\(^ {34,35}\)). Stability increases with atomic number, allowing HREE to be preferentially retained in solution as carbonate ions\(^ {25}\). The distribution of REE along this ‘pH barrier’ is heterogeneous and the REE can be concentrated in lenses or in micropores, space fillings and microveins\(^ {14}\).

**Fe content:** Fe-rich goethite has a significant scavenging effect, preferentially fixing mobile REE, in particular the LREE, within residual Fe-rich layers\(^ {36}\). Positive correlations exist between \(\text{Fe}_2\text{O}_3\) and \(\Sigma\text{REE}\), particularly where Fe oxy-hydroxides occur as ferraligenous ooids (e.g. Olmedo Bauxite, Italy\(^ {25}\)).

**F depletion:** Bauxite is typically depleted in F; this depletion is a critical factor in controlling the type of minerals that form. F can be substituted by -OH groups to form hydroxylbastnäsite as such hydroxylbastnäsite-(Nd), which has been described from
Nikšić in Montenegro. Hydroxylbastnäsites are the most common authigenic REE minerals found in bauxite.

Figure 3: Typical Nd distribution through the Stitovo bauxite, Montenegro (after Maksimovic and Panto 1995 (figure 10.1 chapter 10 p262)\textsuperscript{14}). The enrichment of Nd at the base allows for the formation of authigenic REE minerals such as Nd-goyazite, bastnäsite and hydroxylbastnäsite-(Nd)\textsuperscript{37,28}.

Ce does not have the same per descensum correlation that is observed for the other REE. This is due to the oxidation of Ce\textsuperscript{2+} to Ce\textsuperscript{4+} in the strongly oxidising environment created during bauxitisation\textsuperscript{28,38,39}. This can result in the skewed distribution of Ce within bauxite profiles with Ce enrichment occurring in the upper parts of the bauxite deposit whilst the rest of the REE have been transported downwards.

**Rare Earth Elements in Red Mud**

To separate alumina from bauxite, a processing route known as the Bayer process is employed. Bauxite is digested in a hot sodium hydroxide solution to convert the alumina to aluminium hydroxide, which dissolves in the hydroxide liquor. The other components of bauxite do not dissolve. The solution is clarified by filtering off the solid impurities, which forms the so-called bauxite residue or red mud. The actual composition of red mud depends on the type of bauxite, the mining location and the process parameters of the Bayer Process\textsuperscript{40}. REE content in red mud has been shown to double as a result of the Bayer Process\textsuperscript{11} and this is consistent in both Jamaican and Greek deposits\textsuperscript{10}. Mineralogical studies have shown that in the Jamaican red mud samples the REE are dispersed as ion-adsorbed elements or as an unknown phase associated with iron oxides\textsuperscript{41}. The resource potential of red muds in Europe (including Turkey) is significant with approximately 3.5 million tonnes (Mt) of bauxite ore extracted in 2012\textsuperscript{17}, which resulted in the production of an estimated 140 000 tonnes (t) of red mud waste.
Rare Earth Elements in Greek Bauxites

The karst-bauxite deposits of Greece are among the world’s most important sources of bauxite. Exploitable deposits of bauxites exist mainly in the regions of Mt Parnassus, Mt Giona and Mt Helikon (central Greece) and reserves are approximately 600,000 t – the 9th largest bauxite reserves globally\textsuperscript{42}. Previous research on these deposits includes the quantification of REE and Sc in bauxites and red mud waste\textsuperscript{43,11}, and development of separation techniques for Sc and REE from the red mud\textsuperscript{12}.

Parnassos-Ghiona bauxite

The Parnassos-Ghiona geotectonic zone is characterised by nearly continuous sedimentation of epicontinental reef-like carbonates from the Upper Triassic to the Upper Cretaceous. Bauxites occur in three main horizons (B1–B3) (Figure 4). Geochemical analysis of samples from this region has been conducted in this study and the results are presented below in Figure 5 and Table 1.

\textbf{Figure 4:} Stratigraphic column showing the three bauxite horizons (after Laskou and Economou-Eliopoulos, 2013)\textsuperscript{50}
Figure 5: Plot of average published REE values for each of the three main horizons (B1–B3) and red mud (RM); and preliminary data based on 18 samples taken from three dehydrated red mud waste tips at the Aluminium S.A. site (RM N). Data for mixed bauxite ore (MB) that enters the plant is shown. All values are chondrite normalised using McDonough and Sun 1996. [Data from 33,43,11,45,46,47,48,49,50].

Tsirambides and Filippidis report ΣREE values in the bauxites and lateritic bauxites of central Greece as 3275 to 6378 ppm. Although these values are significant, these concentrations are unlikely to be reflective of all Greek bauxite deposits. High values are likely to result from the sampling of localised areas with REE enrichment along the footwall limestone, and are not representative of average REE concentrations in the bauxite. Chondrite-normalised data for average REE values from the three different bauxite horizons of the Parnassos-Ghiona zone are shown in Figure 5. The combined REE values for bauxite horizons B2 and B3 (Figure 4) were estimated using samples of the mixed throughput ore from the plant at Aluminium S.A., Greece (sample MB). Data compiled for this study indicates an average ΣREE+Y value of ~500 ppm for the bauxite and ~900 ppm for the red mud samples (Table 1). REE concentrations in the collated data indicate variation across the three main bauxite horizons, with a mixture of these horizons entering the processing plant (MB). The two-fold increase in REE in the red muds compared with the original bauxites is consistent with the literature e.g.11.
Table 1: REE values compiled from the literature for B1–3, RM and MB samples. New data is presented as RM N. Samples were analysed for \(\Sigma\)REE+Y content in the geochemical laboratories of the Camborne School of Mines.

The variation in REE concentration between specific horizons, particularly the enrichment observed in B2 is likely to be a function of sampling an enriched zone, which is not necessarily reflective of the entire horizon. The vertical, and probable lateral, variation in REE concentrations illustrate the need for a robust sampling strategy involving the collection of more carefully characterised samples.

**Bauxite as a potential resource**

Production of REE in the form of RE oxides (REO) is currently limited to six countries: Russia, USA, China, Brazil, Malaysia and Australia\(^\text{17}\). With total production of bauxite from Europe (+Turkey) of \(~3.5\) Mt\(^\text{17}\), this results in annual production of \(~140\) 000 t of waste red mud, with an average homogenised REE content of \(~900\) ppm, based on \(\Sigma\)REE+Y from sample RM in Table 1. If these quantities of red muds were processed and REE extracted, it would result in total REE production of \(~1300\) t annually. In a best case scenario, with REE enriched bauxite having an average \(\Sigma\)REE concentration of \(~2000\) ppm\(^\text{14}\), this would result in REE production of \(~2800\) t annually. This is based on REE extracted from the Bayer Process would likely be in the form of oxalates or carbonates, which have a relatively low market value as additional costs are incurred in separating the individual REEs. In Greece, Aluminium S.A. is the largest consumer.
of Greek bauxite, processing over 1.5 Mt annually and producing 700 000 t of red mud waste annually51,52. Deposition of dehydrated waste mud started in 2009. Accordingly the total volume accumulated is approximately 3.5 Mt. Assuming an average $\Sigma$REE of 1000 ppm, if processed this could potentially produce ~3500 t of contained REE. It is notable that the data also show a relatively high content of HREE relative to LREE, which may have economic implications. However, there are challenges associated with the exploitation of red mud waste, specifically the difficulty in controlling REE concentrations. REE concentration varies significantly between deposits and within individual bauxite horizons and this directly affects the REE concentration of the resulting red muds.

**Discussion**

Fully understanding the mineralogy and natural processes of REE enrichment in bauxites is vital to assessing the REE resource potential of bauxites and red muds in Europe. Great variability in both the mineral concentration and composition between and along bauxite horizons is documented44. This means acquiring red muds with consistent REE concentrations to feed a processing plant would be challenging. However, there are occurrences which are more enriched in particular REE, such as the Montenegro deposits at Niksic, which host hydroxylbastnäsite-(Nd) as the predominant REE mineral. Improved understanding of the heterogeneity of REE distribution within the bauxite could allow for the targeting of REE enriched portions of the bauxite. It is likely that once the supply of REE becomes more geographically diverse there will be greater emphasis on acquiring metals from sources with the lowest environmental impact19. Existing stockpiles of red muds could represent a more environmentally sustainable source of REE for Europe as additional mining is not necessary and current “stockpiles” of red mud would be viewed as a resource rather than a waste product with the associated disposal issues.

Although the quantities of REE contained in red muds appear to be low (average ~900 ppm) when compared with primary deposits of carbonatite (e.g. Mountain Pass and Mount Weld have grades of about 80 000 ppm REE53), in a scenario based upon a REE grade of 2000 ppm (~2800 t contained REE) red muds could account for about 10 per cent of EU demand for REE. EU imports of rare earths in 2011 (REE+Y+Sc metals and compounds) totalled ~26 500 t54.

More significantly, it may contribute to improving security of supply for some REE to the European market. European production of REE in high demand would ensure a secure supply source and remove some of the risks associated with the importation of REE from geopolitically unstable countries.

The economic viability of REE production from European red muds needs careful assessment due to the investment required in mineral processing and extraction technology. Further research focused on improved characterisation of red mud
stockpiles, selective mining of REE enriched bauxites, and the development of efficient REE recovery techniques from red muds is required to fully assess these potentially important resources.

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THE IMPORTANCE OF TECTONIC SETTING IN ASSESSING EUROPEAN RARE EARTH POTENTIAL

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Abstract

Rare earth element (REE) resources are commonly found associated with alkaline igneous complexes or carbonatites, or as secondary deposits derived from igneous rocks. Globally, many REE deposits occur around the margins of Archaean cratons, most in continental rift zones. Europe contains many such rift zones, which are generally younger in the south. Many of these rifts are intracontinental, whereas others are associated with the opening of oceans such as the Atlantic.

All these rift systems have the potential to host REE resources, but whereas the older provinces of northern Europe are deeply exposed, exposures in southern Europe are largely at the supracrustal level. This paper considers how an understanding of the tectonic setting of Europe’s REE resources is vital to guide future exploration.

Introduction

Although the rare earth elements (REE) can be concentrated by geological processes in a range of tectonic settings, the most significant concentrations are typically associated with alkaline-peralkaline silicate rocks and carbonatites formed in extensional intracontinental rifts. Such rifts are found in all the continents, dating from the Archaean to the present day. However, the ultimate source of alkaline and carbonatitic magmatism within the rifts remains controversial: one hypothesis states that the emplacement of these magmas is largely controlled by structures in the underlying lithosphere, whilst the contrasting view invokes a role for mantle plumes.

This controversy is of the utmost importance for REE exploration. If mantle plumes are the most important control, REE enrichments could potentially be found anywhere – even in ocean islands. Alternatively, if the lithosphere is the most important control, it is perhaps more likely that REE enrichments would be focused in areas with long and complex lithospheric histories. This paper will assess alkaline magmatism across Europe in this context, and consider the implications for REE resources.
Intracontinental rifts in Europe

Europe has a long and complex geological history, from the Archaean cratons of Greenland and northern Scandinavia, to volcanic suites around the Mediterranean that are only a few years old. This history comprises several cycles of continental break-up and collision (Wilson Cycles) and thus includes many intracontinental rifts (Figure 1) that represent potential REE metallogenetic belts.

Archaean alkaline silicate and carbonatite magmatism is rare across the globe. In Europe, the main examples date from c. 2700 Ma and include the Skjoldungen alkaline province, Greenland and the Siilinjärvi carbonatite in Finland. Although these are enriched in the REE, as is typical for alkaline magmas, they are considered unlikely to host economic REE mineralisation; Siilinjärvi is currently mined for phosphate.

Figure 1: Map of Europe showing the approximate extent of some of the major alkaline provinces mentioned in the text. Yellow stars indicate important REE deposits. 1: Sarfartoq; 2: Qeqertaasaq; 3: Kvanefjeld, Kringlerne and Motzfeldt; 4: Fen; 5: Norra Kärr; 6: Alnö; 7: Sökli.

By contrast, some of Europe’s most important REE mineralisation is associated with rifts of Proterozoic age. The Gardar Province of south-west Greenland was emplaced along the boundary between the North Atlantic Craton and a Palaeoproterozoic
mobile belt to the south. The province comprises two periods of rift-related magmatism, one at c. 1280 Ma and a second at 1180-1140 Ma\(^6\). Both episodes are characterised by extensive dykes and emplacement of alkaline to peralkaline plutonic complexes. The Motzfeldt centre of the Igaliko complex, and the Ilimaussaq complex, both comprise peralkaline syenites with zones that have been enriched in REE by magmatic and/or hydrothermal processes. The Ilimaussaq complex contains two major REE deposits, Kvanefjeld and Kringlerne. Other syenitic and carbonatitic complexes within the Gardar Province are the focus of current REE exploration.

In Fennoscandia, the Mesoproterozoic was a time of complex accretionary tectonics, with collisional zones separated spatially and temporally by localised rifting and magmatism. Episodic rift-related magmatism occurred within Fennoscandia throughout much of the Mesoproterozoic\(^7\)\(^-\)\(^8\), although distinct rift-related igneous provinces have not been identified. Examples of alkaline intrusions formed at this time include the Norra Kärr and Almunge syenites in southern Sweden, of which the former is recognised as an important HREE-enriched deposit.

Although the Neoproterozoic and early Palaeozoic were marked by rifting in Europe as the supercontinent Rodinia broke up, there is relatively little evidence of alkaline magmatism at this time. The exceptions are zones of carbonatite and lamprophyre intrusion in Greenland and Scandinavia. In west Greenland, one such zone is dated at 555-605 Ma\(^9\) and includes the Sarfartoq carbonatite which is currently being explored for REE. In Scandinavia, the Fen carbonatite complex in Norway and the Alnø alkaline-carbonatite complex in Sweden have both been dated at c. 580 Ma\(^10\) and are known to contain zones of REE enrichment. Rift-related magmas were also emplaced elsewhere in Europe at this time, but appear to have been strongly affected by crustal assimilation, such that alkaline compositions are rarely seen.

In the aftermath of the Caledonian and Variscan orogenies, rifting and alkaline magmatism developed in many areas across northern Europe. The most dramatic of these rifts is the Kola Alkaline Province, which was emplaced into the Fennoscandian Shield during the Devonian. Notably, this area had been the site of repeated alkaline magmatism during the Precambrian\(^11\). The province comprises a number of alkaline ultramafic, syenite and carbonatite complexes which extend across the Kola Peninsula in Russia and into Finland. The most notable of these within Finland (and therefore in the area reviewed by this paper) is the Sökli phoscorite-carbonatite complex\(^12\), which has been extensively explored for phosphate.

Rifting and alkaline magmatism also developed through the Carboniferous and Permian across the UK, southern Scandinavia (particularly the Oslo Rift), and into northern Germany\(^13\). In the Oslo Rift, exposures include both volcanic successions and
alkaline plutons, some having notable enrichments in the REE. The UK Permo-Carboniferous magmatism in the Midland Valley of Scotland and Northern England is at a higher erosional level, with volcanics, dykes and sills but no plutonic rocks exposed.

The late Mesozoic and Cenozoic represent a major period of rifting in Europe, with alkaline magmas being emplaced in many areas. In western Europe, Mesozoic to Cenozoic rifting associated with the formation of the Atlantic Ocean generated large areas of flood basalt with associated mafic to ultramafic layered complexes that do not have elevated REE concentrations. However, some alkaline and carbonatitic magmatism was generated. The Jurassic Qeqertaasaq and Tikiussaq carbonatites at the margin of the North Atlantic Craton in West Greenland are currently being explored for REE. In east Greenland, the Gardiner Complex is a Cenozoic alkaline ultramafic, syenite and carbonatite intrusion which contains some REE-enriched zones. Plutons of similar age also occur in the UK, but are typically granitic in composition and show only minor REE enrichment. Further south, late Cretaceous (94-72 Ma) alkaline magmatism in the Iberian peninsula produced numerous syenitic intrusions, forming the Iberian Alkaline Province.

Following collision during the Alpine orogeny and subduction around the Mediterranean, Cenozoic rifts and associated alkaline magmatism developed across much of central and southern Europe. North of the Alpine collision zone, the Massif Central in France, the Rhenish Massif and Rhine Graben in Germany, and the Bohemian massif all include alkaline volcanic rocks, including some differentiated compositions. Carbonatites are rare but those that have been identified are of interest for their REE contents (e.g. the Storkwitz project in Germany). Alkaline volcanism also occurs in many areas around the margins of the Mediterranean, particularly in the Roman province of Italy and on Sicily and Sardinia, and in the Pannonian Basin and Anatolian rifts further east. The current level of erosion means that in these areas, the central complexes that might contain significant primary REE resources are still hundreds of metres to kilometres below the surface.

**Magmatism in intracontinental rifts and REE enrichments**

Intracontinental rifting is a key part of the Wilson Cycle, and as such has occurred at many times in the geological history of Europe. The majority of Europe’s largest REE resources are associated with mantle-derived alkaline magmatism in these intracontinental rifts.

The original source of magmas in these rifts is in many cases the subject of debate; some authors suggest derivation from mantle plumes, some from the sub-continental lithospheric mantle, and some from the convecting asthenosphere. Whilst the
contribution from mantle plumes typically remains uncertain, it is likely that most continental rifts include magmas sourced both in the lithospheric mantle and in the deeper asthenospheric mantle. However, it is notable that alkaline magmatism develops repeatedly in certain areas, often where major lithospheric structures provide pathways for magma to rise up into the crust. In these areas, the lithospheric mantle keels are also likely to have been enriched in a range of elements through repeated metasomatism associated with fluids rising from subducting slabs.

Figure 2: Schematic diagram illustrating development of lithospheric complexity. The left-hand side shows how subduction at the margins of a craton with thick lithospheric keel will introduce magmas and fluids, carrying a range of elements, into the overlying crust and lithospheric mantle. The right-hand side shows how subsequent extension of this complex lithosphere may produce alkaline magmatism derived from asthenospheric and metasomatised lithospheric sources.

In Europe, the most important such areas include the margins of the North Atlantic Craton in Greenland and the margins of the Fennoscandian Shield in Scandinavia. It is these areas that contain the most significant currently identified European REE deposits. However, repeated orogenic cycles since the Precambrian have developed the same level of lithospheric complexity in southern and central Europe, providing a basis for the Cenozoic alkaline magmatism in these areas. In these younger provinces, the plutonic counterparts to the surface volcanics are rarely exposed.

To summarise, the principal REE metallogenetic belts in Europe are those in which alkaline magmas have been emplaced, during extension, into zones of complex continental lithosphere that offer both a range of magma sources and structural
pathways for magma to rise into the crust. REE are typically concentrated in plutonic rocks and thus near-surface resources are found in the more deeply eroded alkaline provinces of northern Europe. However, it is very likely that comparable primary REE resources remain to be discovered at depth within southern Europe's younger rift provinces.

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THE PALAEOPROTEROZOIC SKARN-HOSTED REE MINERALISATIONS OF BASTNÄS-TYPE: OVERVIEW AND MINERALOGICAL – GEOLOGICAL CHARACTER

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Abstract
The Bastnäs-type rare earth element (REE) deposits are located in the Palaeoproterozoic Bergslagen ore province in the Swedish part of the Fennoscandian Shield. These deposits comprise magnetite-skarn-hosted REE silicate mineralisations that occur along a discontinuous belt, c. 100 km in length, hosted by metamorphosed c. 1.90-1.87 Ga Svecofennian volcanosedimentary rocks. The major REE-minerals are LREE-enriched silicates, e.g. cerite-(Ce), and carbonates, e.g. bastnäsite-(Ce). Available evidence suggest that the Bastnäs-type deposits formed through replacement reactions between c. 1.9 Ga carbonate units and hydrothermal, magmatic-dominated fluids, most likely related to volcanic-subvolcanic activity coeval with the younger parts of the host rock sequence. Despite their known relatively small sizes, several are studied by exploration companies.

Introduction
The increasing global interest in rare earth elements (REE) and their deposits has prompted both new exploration as well as renewed interest in known occurrences. Overall, the Nordic part of the Fennoscandian Shield is considered one of the areas with highest potential for exploration in Europe today, not least for iron, base and noble metals. In addition, several projects for rare and critical metals including the REE are presently in different stages of development. Advanced REE projects include the syenite-hosted Norra Kärr deposit in southern Sweden¹. Yet, the most classic of REE-rich mineralisations in the Shield are the skarn-hosted deposits of Bastnäs-type, in the Palaeoproterozoic Bergslagen ore province of south central Sweden (Fig. 1). The element cerium was discovered in cerite-(Ce) from the Bastnäs mines², and a succession of early studies led to the discovery of additional new elements and minerals. Subsequently, a number of similar deposits were identified in the west central part of the province, and brought together under the classification “Bastnäs-type deposits”³. Active during the 1800s, the mines of the Bastnäs field were most
likely the first hard-rock deposits ever mined explicitly for REE extraction. Still today, the abundant mine dumps exhibit mineralised material, typically with significant REE contents (Table 1).

Over time, the Bastnäs-type deposits have been debated both as to their formation and relations to host rocks and other types of mineralisation. Their genesis, together with that of the associated skarn iron ores and the extensive host-rock alteration, was originally interpreted to be related to large-scale, so-called magnesia metasomatic processes, generated by granitoids emplaced at the waning stage of regional metamorphism. Presently hydrothermal scenarios are favoured, involving reactions between magmatic-hydrothermal fluids and pre-existing limestone layers.

REE mineral names are mostly given with recommended Levinson modifiers (Table 2). Where detailed mineral chemical information is lacking, this is not applied. Occurrences of what is referred to as “orthite” in older literature, and where sufficient data is not available, are represented here by “allanite”, as “orthites” reported from this area have been shown to represent an array of different species.

### Table 1: Whole rock REE concentrations in mine dump samples, Bastnäs-type deposits.

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<th>Locality</th>
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Concentrations of Ce, La, Nd, Pr > 10000 ppm, Gd, Dy, Er > 1000 ppm were analysed by ICP-AES. All other elements were analysed by ICP-MS at ALS, Vancouver, Canada.

### Table 2: REE-minerals in the Bastnäs-type deposits.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>General formula</th>
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<tbody>
<tr>
<td>Allanite (Ce)</td>
<td>Ca(Ce,REE)Fe₆⁺Al₂(SiO₄)₂(Si₂O₇)(OH)ₓ</td>
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<tr>
<td>Bastnäsite (Ce)</td>
<td>Ca(Ce,REE)CO₃F</td>
</tr>
<tr>
<td>Bastnäsite (La)</td>
<td>La(Ce,REE)CO₃F</td>
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<tr>
<td>Cerianite (Ce)</td>
<td>Ca(Ce,REE)O₂</td>
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<tr>
<td>Cerite (Ce)</td>
<td>(Ce,REE)Ca₂(CO₃)₂F</td>
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<tr>
<td>Dissakite (Ce)</td>
<td>Ca(Ce,REE)Mg₂Al₂Si₅O₁₁(OH)₂</td>
</tr>
<tr>
<td>Dollaseite (Ce)</td>
<td>Ca(Ce,REE)Mg₂Al₂Si₅O₁₁(OH)₂</td>
</tr>
<tr>
<td>Ferrialanite (Ce)</td>
<td>Ca(Ce,REE)Fe₅⁺Al₂(SiO₄)₂(Si₂O₇)(OH)ₓ</td>
</tr>
<tr>
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<td>La(Ce,REE)F</td>
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<td>Fluorbritholite (Ce)</td>
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<td>Gadolinite (Ce)</td>
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<td>Tornbohmite (Ce)</td>
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</tr>
<tr>
<td>Västmanlandite (Ce)</td>
<td>Ca(Ce,REE)F</td>
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</table>

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**Geological setting**

The REE-line is located in the western part of the Palaeoproterozoic Bergslagen ore province in the c. 1.9-1.8 Ga Svecokarelian orogen (Fig. 1). Archaean and older Palaeoproterozoic rocks outline the northeastern boundary of the orogen, and to the south and southwest it is succeeded by the 1.85-1.65 Ga Transscandinavian Igneous Belt.

During the Svecokarelian orogeny the Palaeoproterozoic rocks in the Bergslagen province formed in a back-arc setting inboard of an active continental margin. The oldest, 1.90-1.87 Ga rocks, belong to a volcanosedimentary succession with coeval intrusive rocks. Polyphase deformation and LP-HT greenschist to amphibolite facies metamorphic occurred between c. 1.85 and 1.80 Ga. A suite of younger intrusive rocks was

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**Figure 1:** Geological overview map of the Bergslagen ore province, south central Sweden. Inset map shows the Bergslagen province and its position in the Fennoscandian shield (left). Geological map showing the major deposits of the REE-line, the linear occurrences of Bastnäs-type deposits in west central Bergslagen (right).
emplaced after the main deformation stage and are dominated by granites and associated pegmatites. The succession of metavolcanic rocks is estimated to be c. 8 km thick, and are mainly of rhyolitic to dacitic compositions, with subordinate occurrences of mafic rocks. The felsic metavolcanic rocks, typically with intercalated marbles and associated skarns, host most of the base metal and iron oxide mineralisations in the province\(^4,12\), including the Bastnäs-type deposits. 

The REE-line (Fig. 1) stretches about 100 kms in a NE-SW direction with a moderately to steeply dipping foliation, and is interpreted to be located in the core of an antiform\(^13\). It hosts a number of groupings of REE-rich iron skarn deposits with associated BIF occurrences, as well as similar mineralisations without elevated REE contents. The mineralisations follow marble horizons interlayered with the metavolcanic rocks. Near the skarn deposits these rocks were strongly hydrothermally altered, and subsequently transformed during regional metamorphism into cordierite and/or andalusite-bearing mica schists or quartzites\(^14,15\). Meso-scale, ductile folds have been recorded along the REE-line\(^7\) and the mineral assemblages in the deposits are recrystallised, indicating that they were formed at an early stage of the orogenic evolution. Mining of the iron oxide deposits in this area was active from the Middle Ages and into the 1980s.

### The Bastnäs-type deposits

The iron oxide skarn-associated REE silicate mineralisations occur within a specific sequence of the altered metavolcanic rocks, and they have been separated into subgroup 1 and 2 based on their location and their mineralogy and geochemistry\(^9\). Subtype 1 includes more iron-rich silicates and mainly LREE enrichment and subtype 2, exhibiting more magnesium and fluorine-rich silicates and enrichment in both LREE and Y+HREE. Their complex and diverse REE mineralogy and the variability between deposits is shown in Tables 2 and 3.

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**Table 3: Observed REE minerals in the bastnäs-type deposits.**
The Nora area
Two occurrences are known from the Nora area (Fig. 1). The predominant REE-assemblage at Rödbergsgruvorna consists of cerite-(Ce), allanite-Ce – ferriallanite-(Ce), bastnäsite-(Ce), and a västmanlandite-like mineral, in clinoamphibole skarn associated with magnetite and minor sulphides\(^6\). REE mineralisation at the Östra Gyttorp mine occurs in the form of allanite-(Ce)-dominated lenses associated with magnetite ore, hosted by felsic metavolcanic rocks\(^6\). During mining, approximately 100 tons of “allanite”-dominated rare earth ore was produced and sold during the late 1800s, beside the iron ore\(^12\). Minor occurrences of “allanite” as well as other REE minerals have been noted in the greater Nora area, in addition to the deposits of Bastnäs-type.

The Riddarhyttan area
The Riddarhyttan area (Fig. 1) includes the most well-known deposit of this type, in the form of the eponymous Bastnäs mines. However, REE mineralisation in this area occurs also at several other locations within the same, partly altered, metavolcanic unit\(^14,15\). The Nya Bastnäsfältet is composed of two parallel ore horizons, featuring skarn-hosted (polymetallic) ores with locally abundant REE minerals, and banded iron formations, respectively (Fig. 2). The former are magnetite-dominated, and occur as pods in mainly clinoamphibole-dominated skarn, wholly or partly replacing marble. In the western part of the Bastnäs field unreacted portions of the marble bed are present.

Rich REE mineralisation was encountered at Ceritgruvan (the cerite mine; Fig. 2). The REE deposits here are of characteristic magnetite-skarn type, but with locally significant Cu-Co-Ni-Bi-Mo sulphides as well as minor Te, Hg-bearing minerals\(^18\) and gold-silver alloys. At Bastnäs the most characteristic REE mineralisation type comprises either only “allanite” (ferriallanite-(Ce)), or an assemblage of cerite-(Ce) and ferriallanite-(Ce), with variable amounts of bastnäsite-(Ce) and törnebohmite-(Ce). It is stated that the overall REE ore production from the Cerite mine was c. 4500 tons, of which cerite alone accounted for several hundreds of tons\(^14,19\). Later reworking of the old dumps at Nya Bastnäs yielded significant additional amounts (B. Högrelius, pers. comm.).

Storgruvan is another REE mineralisation comprising cerite associated with “allanite” and törnebohmite where c. 5 tons of REE-mineralised material were separated and sold\(^14\). The Högfors field to the NE features REE mineralisation within a banded iron formation\(^3,7\), with sparse bands dominated by cerite-(Ce), a västmanlandite-type mineral, ferriallanite-(Ce) and gadolinite-(Ce) as well as additional minor minerals that occur as fine-grained, recrystallised assemblages in folded bands or layers\(^7\).

Outside of this major, ore-bearing unit, REE mineralisation was also encountered at Lerklockan, Stålklockan, Myrbacksfältet and others. Additional REE-mineralised zones
at depth in the greater Bastnäs area were noted during exploratory drilling for gold and base metals in the 1980s.\(^\text{15}\)

![Figure 2: Detailed geological map showing the relations in the Bastnäs ore field, Riddarhyttan. Modified after Geijer\(^\text{14}\).](image)

### The Norberg area

The major occurrences of Bastnäs-type REE mineralisation in the Norberg area (Fig. 1) are the Östanmossa, Malmkärra, Johanna, Åsgruvan and Södra Hackspik mines, all of them magnetite-dominated, magnesium-rich skarn iron ore deposits. The relative abundance of fluorine in the Norberg area deposits (subtype 2) is manifested by the abundance of humite-group minerals, including norbergite. These occur intimately with REE mineralisation, such as at Johanna, where norbergite is present as subhedral crystals included in REE silicates. The presence of humite-group minerals is also indicated by the common occurrence of “ophicalcite”; a carbonate rock containing pseudomorphs of humite-minerals.

The Malmkärra mines are magnetite skarn deposits occurring within a narrow layer of marble. Here, REE mineralisation in the form of fluorbritholite-(Ce), västmanlandite-(Ce) as well as REE-carbonates\(^\text{9,20}\) occurs in a skarn zone in that marble at the contact towards cordierite schists. In the Johanna mine magnetite mineralisation is associated with tremolitic skarn with “ophicalcite” pods\(^\text{21}\), and associated REE mineralisation in the form of dollaseite-(Ce) associated with sparse cerite-(Ce), REE-carbonates and gadolinite-group minerals. At Åsgruvan, another magnetite skarn deposit in marble, carries sparse REE mineralisation, mainly as “allanite”\(^\text{21}\). The mines at Östanmossa...
were operated on a magnetite mineralisation similar to that at Åsgruva

21, but feature more abundant REE mineralisation as dollaseite-(Ce) and fluorbritholite-(Ce), characteristically associated with norbergite9,16,21. The Södra Hackspik mine is another deposit in fluorine-rich skarn, featuring locally REE-rich assemblages, with cerite, törnebohmite, dissaksite-(Ce), dollaseite-(Ce), bastnäsite-(Ce and La), and fluorbritholite-(Ce)9,9,16. In addition, REE enrichment, mainly hosted by “allanite” and REE-enriched epidote has been noted in a number of other iron and base metal mineralisations, such as Stripåsen.

The deposits forming the northeastermmost continuation of the REE-line are not represented in Fig. 1, as they are located significantly farther to the east, yet decidedly forms an offset part of this structure. At Knutsbo, Danielsgruva and Hagruva have been noted for their REE contents, with e.g. "allanite" and törnebohmite described from a talc-bearing amphibole skarn.

Discussion and conclusions

The Bastnäs-type deposits represent a style of mineralisation without directly similar deposits occurring outside of the Bergslagen province. All available evidence suggest that the Bastnäs-type deposits formed as a consequence of submarine volcanic to subvolcanic, magmatic-dominated hydrothermal activity at around c. 1.9 Ga. The iron ores and the associated skarn as well as REE mineralisation were generated through reactions between pre-existing marble beds within the volcanosedimentary sequence, and hydrothermal fluids, most likely in a sub-seafloor position. The differences in mineralogy between the deposits may originate both from local fluid (and mineral) evolution, the degree of fluid-rock interaction9, as well as in variations in the local ore-forming systems, including volcanic-hydrothermal facies.

Despite the modest known size of individual Bastnäs-type deposits, their high grades and extended distribution along the REE-line suggest relevant exploration potential, not least when considering the presence of other metals. A potential problem for the beneficiation of these deposits is their mineralogical complexity. Yet, in most cases, a few REE silicates (e.g., cerite-(Ce), dollaseite-(Ce), ferriallanite-(Ce), fluorbritholite-(Ce)) tend to dominate, which may improve their chances of utilisation.

References

17. G. Nordenström, "Fynd af allanit (cerin) vid Gyttorp i Nora Bergslag" (in Swedish), Geologiska Föreningens i Stockholm Förhandlingar, 12 540-4 (1890).
REE behaviour in hydrothermal alteration zones, Sungun porphyry-Cu deposit, NW Iran

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Abstract

Sungun porphyry-Cu deposit is located in northwest Iran and is a part of Urumieh-Dokhtar magmatic arc. Porphyry type mineralization is related to the Miocene monzonite-quartz monzonite and diorite-granodiorite intrusive rocks. There are four distinguished alteration zones in the Sungun deposit which nearly envelope the ore body. This research is about the behaviour of REE in the potassic, phyllic and argillic zones with regard to indicated geochemical patterns and economic potential. Geochemical characteristics of trace elements show many similarities between alteration zones. There is an obvious LREE enrichment and HREE depletion in the three alteration zones. Eu anomaly in the potassic zone is weakly negative, and in the phyllic is nearly positive, but in the argillic zone there is no Eu anomaly shown up. The lower ratio of Ce/Ce* in the potassic and the respectively higher ratio in the phyllic and argillic zones reveal prevailing reduced and oxidized conditions. Similar physicochemical conditions such as pH, suitable complexes in fluids, and presence of secondary minerals for REE uptake, have contributed to the evolution of the three alteration zones.

Introduction

Sungun-Ahar metallogenic region is part of Alpian-Himalayan orogenic belt. Urumieh-Dokhtar volcano-plutonic belt is extended from NW to SE Iran having a length of 1600 Km and a width of 20 Km. This belt includes volcanic, pyroclastic and intrusive rocks with calc-alkaline type magmatic affinity. It hosts many Cu-Mo porphyry deposits i.e. Sungun.

Many studies have focused on mobility, fractionation and solubility of REEs in hydrothermal systems (Fulignati et al. 1999). According to Rollinson (1993) during low grade metamorphism, weathering and hydrothermal alteration REEs are relatively immobile, except in the cases of high fluid/rock ratios (Michard, 1989). REE mobility can be favoured by pH, fO2, P-T conditions, and availability of SO4, PO4, F, CO3 and OH- ligands (Rolland et al., 2003). In this work the REE behaviour in relation to different hydrothermal alteration zones has been investigated. Also a better understanding of the physico-chemical conditions during hydrothermal alteration is considered.
**Geological setting**

Sungun porphyry copper deposit is located in the central Iranian magmatic arc. The porphyry host rock is a quartz monzonite stock which has been intruded by NNW-SSE and NNE-SSW orientated andesitic dikes. The Sungun porphyry is Oligo-Miocene in age, and was emplaced as a sub-volcanic complex into upper Cretaceous carbonate rocks (Calagari, 2004, Mehrpatou, 1993) (Fig. 1). The hydrothermal alteration zones are distinguished to potassic, phyllic, argillic, and propylitic ones (Calagari, 2003, Hezarkhani, 2006, Mehrpartou and Tarkian, 1999). A series of late Tertiary Quaternary sub volcanic rocks including, latite, quartz latite-andesite were intruded into sedimentary rocks (Calagari, 2004).

**Petrography**

On the basis of petrographic studies, alteration is widely developed in the area. Quartz and sericite are the predominant mineral phases. Potassic alteration zone is taken place in the upper parts of the stock but makes the deepest alteration zone related to the porphyry-Cu mineralisation. Associations of K-feldspar, primary biotite, secondary biotite, sericite, plagioclase, quartz, anhydrite, sphene, muscovite, actinolite and zircon are characteristic minerals of this zone, along with common features of porphyry and granular textures are common (Fig. 2a, b).

Biotite and amphibole were replaced by muscovite as pseudomorph. Rare jarosite in this zone is produced by meteoric oxidation of pyrite (Fig. 2c, d). Jarosite itself is partly altered to goethite (Pirajno, 2009).

Phylllic alteration replaces the potassic zone, by K-feldspar being altered to sericite and clay minerals, and plagioclase altered to sericite. The mineral assemblage includes: plagioclase, sericite, quartz, orthoclase, pyrite, zircon and apatite. The intergrowth texture of mica minerals can be seen as lepidoblastic texture. In the argillic alteration zone, metasomatism is very intense, and primary minerals are altered to
clay minerals. Quartz is the only relict mineral in this zone. Propylitic zone is characterized by chlorite, epidote, calcite and albite.

**Petrology**

Geochemical data of intrusive and altered rocks are shown in the table 1. Using SiO2/(Na2O+K2O) diagram (Middlemost, 1994), Sungun intrusive rocks are diorite, granodiorite and quartz monzonite in composition.

On the basis of TAS diagram (Irvin and Baragar, 1971) the magmatic series shows sub-alkaline affinity, whereas when using AFM diagram (Irvin and Baragar, 1971), the magmatic nature is calc-alkaline. Regarding the Y/Nb discrimination diagram the tectonic setting of the area (Pearce, et al. 1984) is determined to be dominated by volcanic arc granitoids.

**Geochemistry**

Behaviour of major and trace element during the alteration processed were determined by using enrichment-depletion diagram. The mean SiO2 values are 58.82%, 63.91%, 70.71% and 67.38% in unaltered rock, and the potassic, phyllic, and argillic zones respectively. The highest SiO2 content belong to phyllic and the lowest one to potassic altered rocks. K2O and MgO contents tend decreasing from the potassic to phyllic zones (Fig. 3).

Arsenic is an indicator for mineralization and has a magmatic origin. This element could be associated with Cu and Mo. In the potassic zone Cu value ranges between 5160 to 1400 ppm. Also there is a positive correlation between Mo-As and Cu- As (Fig. 4-a, b). Molybdenum content in the potassic and phyllic zones is higher than in the argillic one. Cu and Ag show negative correlation (Fig. 4-c). There is positive correlation between Cu/Ag ratios in all of alteration zones (Fig. 4-d).

**Trace and rare earth geochemistry**
REE patterns of unaltered and hydrothermal altered rocks were normalized to the chondrite value (Fig. 5), aiming at to assign the possible fractionation process, during hydrothermal alteration: (La/Sm)n, (La/Yb)n and (Tb/Yb)n ratios of the altered rocks were compared to unaltered ones (Fig. 6).

The enrichment of light REE (LREE) relative to heavy REE (HREE) in the alteration zones was shown by (La/Yb) n ratio (Fig. 6). ∑REE in the potassic (∑REE= 219.9), phyllic (∑REE= 186.41) and argillic (∑REE=200.5) are higher than in the unaltered rocks (∑REE= 132.89).

The ∑REE in the potassic (219.9) is more than in the phyllic zone (186.41). Decreasing of REE from phyllic to potassic zones is attributed to increasing of water/rock ratio, and decreasing pH (Pirajno, 2009).

The Eu/Eu* ratio of unaltered and altered rocks, is lower than 1, which may depend on the weak Eu anomaly. The negative Eu anomaly is due to plagioclase alteration and also the low fO2 and high CO2/H2O.

Eu can be concentrated with oxide and sulfates phases during hydrothermal process. Due to the presence of sulfide phases, like as pyrite, in the phyllic zone, higher Eu/Eu* ratios would be expected. The Eu/Eu* value of 0.89, in the argillic zone is very similar to that of unaltered rocks (0.94), implying that Eu is immobile during the alteration process. Using (La/Sm) n for LREE/HREE fractionation, (La/Sm)n ratio in the argillic, potassic and phyllic zones are 8.44, 8.21, and 7.29 respectively. The potassic, phyllic and unaltered rock samples show (Tb/Yb)n 2.45, 3.03 and 1.34 respectively, whereas this ratio is 8.28 in the argillic zone. The (La/Yb)n is 69.95 in the potassic zone and 62.45 in the phyllic one which are higher than corresponding value in unaltered rock samples (20.96) (Fig. 6D). It is there by concluded that there is an enrichment of LREE compared to HREE in the potassic and phyllic zones. The high enrichment of LREE relative to HREE in the argillic zone is probably due to clay minerals present. The Ce/Ce* value of 0.96 in the phyllic and 96.5 in argillic zones, reflect oxidized conditions in the hydrothermal systems (Rollinson, 1993) (Fig. 6E). Slightly decreased values of Ce/Ce* (0.95) in the potassic zone implies to prevailed reduced conditions. Potassic alteration zone is characterized by alkaline pH and reduced conditions.
Regarding to Wandlandt and Harrison (1979) mobility of REE and fractionation of LREE/HREE are related to sulfate complexes and increasing water/rock ratio. It seems that sulfate ions can be the most important complexing agents in the fluids (Wood, 1990, Lewis et al. 1998). The enrichment of LREE and depletion of HREE is the main characteristic of potassic zone (Pirajno, 2009). The solubility of REE in the hydrothermal systems is related to the fluid/rock ratio and availability of carbonate complex.

The depletion of HREE with respect to LREE is present in the Sungun samples. This is indicated by F- ion, which preferentially removes HREE during alteration (Lewis et al. 1997, Fulignati et al., 1999). Also the enrichment of LREE in the phyllic and potassic zones is due to SO4^{2-} agents which preferentially make complexes taking up LREE (Lewis et al. 1997). LREE complexes are more unstable than HREE, so these are entering faster into secondary minerals.

**Conclusion**

The Sungun porphyry copper deposit is a part of Alpian-Himalayan metallogenic belt. Porphyry mineralization is related to the Miocene monzonite-quartz monzonite and diorite-granodiorite intrusions.

The deposit is characterized by four alteration zones: potassic, phyllic, argillic and propylitic. REE patterns in the alteration zones are similar to fresh rocks, with all samples showing enrichment of LREE and depletion of HREE. The present of OH^-, F^- complexes caused depletion of HREE in the alteration zones. The F^- ligand is related to the mica minerals like biotite. ΣREE in the phyllic zone is higher than potassic one, which is attributed to the H+ agent and high fluid/rock ratio.

The negative Eu anomaly in the potassic zone is due to reducing fluid and alteration of plagioclase. Negative Ce/Ce* anomaly also confirms the reducing conditions.

The ratios of Eu/Eu* and Ce/Ce* in the phyllic zone is higher than potassic one, due to high oxidized conditions. The highest LREE/HREE fractionation is shown in the argillic zone which relates to the high H+ activity and the presence of secondary minerals for the uptake of these elements.
References:

Figure 1: Geological map of the Sungun porphyry-Cu deposit, (Hezarkhani, 2006), and location in the Sahand-Bazman belt.

Figure 2: a) Microgranular texture in the potassic zone, b) Pesudomorph and relict textures in the potassic zone, c) association of jarosite and muscovite in the potassic zone, d) Late alteration of jarosite to goethite.
Figure 3: Enrichment-depletion diagrams of major elements in the a) potassic, b) phyllic and c) argillic zones.

Figure 4: Variation binary diagrams:  a) As versus Mo, b) As versus Cu, c) Ag versus Cu and d) Cu/As versus Cu/Ag in the potassic, phyllic and argillic zones.
Figure 5: REE pattern diagrams for potassic, phyllic, argillic altered zones in comparison with corresponding patterns of unaltered host rocks.

Figure 6: Modified variation binary diagrams of a) Eu/Eu*, b) La/Sm, c) Tb/Yb, d) La/Yb and e) Ce/Ce*, which are indicated of REE differentiation during hydrothermal alteration process from intrusive rock to altered rocks.
RARE EARTH ELEMENT SIGNATURES IN MANGANESE ORES ASSOCIATED WITH TETHYAN OPHIOLITES, IRAN; INDICATORS OF PRIMARY ORE FORMING PROCESSES

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Abstract

The ophiolitic rocks along the Zagros orogenic and metallogetic belt, a segment in the western part of the Tethyan collisional zone, are characterized by the widespread occurrence of manganese and ferromanganese deposits. These deposits are closely associated with radiolarian cherts and basaltic rocks, which cap the ophiolite sequences. The present work provides a set of Rare Earth Element (REE) data for the manganese-bearing layers and nodules of three of these deposits: the Nasirabad and Abadeh Tashk manganese deposits (associated with the Neyriz ophiolite) and the Gugher manganese and ferromanganese deposit, associated with the Baft ophiolitic mélangé. The data are used to elucidate the primary processes that control the deposition of manganese ores. Low REE contents, positive Eu anomalies and La₃/ND₃ ratios (˃3) indicate a proximal hydrothermal source for the Gugher and Abadeh Tashk manganese and ferromanganese deposits. In comparison a relatively low REE abundance, negative Eu anomalies and position on a La₃/CE₃ versus Al₂O₃/(Al₂O₃ + Fe₂O₃) discrimination plot indicate a distal hydrothermal source for the Nasirabad ore-bearing layers and nodules. Moreover a weak positive Ce anomaly and elevated Ce/La values indicate the contribution of terrigenous materials in the formation of Nasirabad ore-bearing layers. Finally, the comparison of the Gugher, Abadeh Tashk and Nasirabad manganese and ferromanganese deposits with other manganese deposits elsewhere in the world indicate that the REE patterns of Zagros manganese deposits are analogous to those typical of hydrothermal deposits.

Introduction

More than 45 manganese deposits of economic importance have been reported in Iran [1]. These deposits have diverse origins and geological settings, and range in age from Precambrian/Early Cambrian to Late Miocene-Pliocene [1, 2, 3]. Many of these manganese deposits lie within the Zagros orogenic and metallogetic belt, which is located in the western part of the Tethyan collisional zone. This belt contains excellent
exposures of ophiolite sequences, including the Naien, Shahr Babak, Baft, Neyriz and Kermanshah ophiolites (Fig. 1). The manganese deposits are commonly associated with radiolarian cherts and basaltic rocks, capping the ophiolite sequences; examples of such deposits include Abadeh Tashk, Nasirabad (associated with the Neyriz ophiolite), Kamyaran, Sorkhvand (associated with the Kermanshah ophiolites), Gugher and Gushk (associated with the Baft ophiolites). The present paper provides a set of REE data for the manganese-bearing layers and nodules of the Nasirabad, Abadeh Tashk and Gugher manganese and ferromanganese deposits. The data are used to provide a general overview of the primary processes that control the deposition of manganese ores.

Figure 1: Map showing locations and distribution of different ophiolite complexes in Zagros orogeny and the location of the Nasirabad, Abadeh Tashk and Gugher manganese and ferromanganese deposits. Modified after Ghasemi and Talbot [4], Abbreviations; Kh: Khoy, Kr: Kermanshah, Ny: Neyriz, Ba: Baft, Sh: Shahre-Babak, Na: Nain.

Geological setting
The Zagros orogenic and metallogenic belt can be divided into three main tectonic trends, namely, the Zagros Fold and Thrust Belt (ZFTB), the Sanandaj-Sirjan Metamorphic Zone (can be subdivided into the north and south SSZ), and the Urumieh-Dokhtar magmatic arc (UDMA)[5]. The ophiolitic rocks along the Zagros orogenic belt are classified into two groups of different ages: the Nain-Shahr Babak-Baft ophiolite belt and the Neyriz-Kermanshah ophiolite belt [4]. The former belt is a remnant of the Naien-Baft palaeo-ocean that existed along the northern margin of the South SSZ.
before the end of the Cretaceous, and the Neyriz-Kermanshah ophiolite belt is a remnant of the Neo-Tethys ocean that was closed during the Miocene (Table 1). The locations of the Nasirabad, Abadeh Tashk and Gugher manganese and ferromanganese deposits are shown in Fig. 1.

**Table 1:** The age (formation) and main characteristics of Zagros ophiolitic complexes

<table>
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<tr>
<th>Ophiolitic Rocks</th>
<th>Formation Age (Ma)</th>
<th>Characteristics</th>
</tr>
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<td>Neyriz</td>
<td>93–95 Ma (Ar/Ar)</td>
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<td>Nain</td>
<td>99–101 (Ar/Ar)</td>
<td>Harzburgite-Iherzolite, small ocean basin around Lut Block</td>
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<td>Shahr-e-Babak</td>
<td>93 Ma (Ar/Ar)</td>
<td>Harzburgite-Iherzolite, small ocean basin around Lut Block, IAT</td>
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</tbody>
</table>

from Ghazi [⁶].

The Nasirabad manganese occurrence is located to the south of the Neyriz ophiolite. In this region the extremely folded and fractured ore-bearing layers and manganese nodules occur as interlayers with reddish radiolarites in the upper parts of the Pichakun zone. This zone represents the Late Triassic to Middle Cretaceous abyssal facies of the Neo-Tethys ocean basin. It is thought that the Neyriz ophiolite has been thrust over the Pichakun zone [⁷]. The lower parts of this zone are composed of Upper Triassic megalodon limestone turbidites, dark marl, and serpentinite diapirs. These grade upwards into thinly-bedded (<5 cm) cherty radiolarites, alternating with medium-to-thick-bedded (up to 5 m) detrital limestone and green siliceous shale. Above this lies a 500 m-thick sequence of radiolarites. Radiolarites of the upper parts, which host the manganese mineralization, are younger than Middle Jurassic in age [⁸]. Finally, the anhydritic limestone of the Tarbur Formation (Campanian-Maastrichtian) unconformably overlies the radiolarites.

The Abadeh Tashk manganese deposits are located to the NE of Tashk lake between 29° 47′-55″ N and 53° 45-56″. In this region, the exposure of the Neyriz ophiolite sequence is not complete. The ophiolite forms a discontinuous linear outcrop belt about 16 km long and 11 km wide, between the high Zagros and the main Zagros thrust fault (Fig. 1). Mn-mineralization in Abadeh Tashk is associated with radiolarite cherts, belonging to the Late Triassic to Early Cretaceous [⁹]. The chert sequences here include both proximal bedded facies, and distal sedimentary facies. However, the bulk of Mn-mineralizations are spatially related to reddish brown radiolarian cherts (part of the proximal bedded facies) that overlie the serpentinized ultramafic rocks of the ophiolite [¹⁰]. These radiolarites are overlain unconformably by massive limestones [⁹].
Abadeh Tashk manganese deposits represent three main textural features, namely, syngenetic, diageneric and epigenetic\textsuperscript{[10]}. The syngenetic textures typically are consist of thinly banded (2-3 cm) and disseminated Mn-minerals (mainly braunite and psilomelane) within the radiolarite cherts interlayers, which cap the pillow lava basalts and serpentinitized ultramafic rocks. In diageneric structures, the re-mobilization of ore minerals during deformation events have been resulted in accumulation of braunite, pyrolusite and bixbyite in fold hinges. Moreover, Mn-mineralization as lenses and boudin are common features of diageneric deposits\textsuperscript{[10]}. The epigenetic features represent the post depositional supergene enrichment processes, within which pyrolusite, rancieite and aurorite were mainly deposited as open-space filling textures in the upper parts of chert sequences\textsuperscript{[10]}.

Comparison of the Neyriz ophiolite with the Baft ophiolite sequences indicates that the latter is strongly imbricated and sheared by closely spaced sub-vertical faults and shear zones. It is referred to as a colored mélange complex\textsuperscript{[11]}. The Baft ophiolitic mélange consists of the following rock units from bottom to top: (1) ultramafic – mafic complex (serpentinitized harzburgite, gabbro, massive diabase, diabase dyke, spilitized pillow lava and basic flow breccia with fragments of spilites), (2) sedimentary units (Cretaceous limestone, sandstone and conglomerates) and (3) metamorphic units that are slabs from the SSZ, tectonically overturned on top of the ophiolitic mélange. These units are mainly composed of calcschist, chlorite-sericite schist (amphibole schist), biotite schist, marble and crystalline limestone of Paleozoic age\textsuperscript{[4, 12]}. The Gugher manganese and ferromanganese ores are located in the northwest of the Baft ophiolite mélange. In these regions pyrolusite, hematite, goethite, pyrochroite, tephroite and Fe-Mn silicate occur as lenticular, layered and sometimes cross cutting veins. These ores are commonly hosted by basalt and iron chert or massive limestone\textsuperscript{[12]}. The indicative textures of sub-marine hydrothermal processes such as cockade (amorphous silica enclosed by Fe-Mn oxyhydroxide shale) and colloform (pyrolusite nucleous surrounded by microcrystalline quartz) have been recognized, and are described in Heshmatbehzadi and Shahabpour\textsuperscript{[12]}.

**Methodology**

From the literature we compiled the data of three manganese deposits, consist of Nasirabad, Abadeh Tashk and Gugher. For the Nasirabad, samples were collected from the manganese-bearing layers, nodules and radiolarian cherts, hosting manganese mineralization. For petrochemical analysis, 5 relatively unaltered and fractured samples from manganese-bearing layers and 3 samples from nodules were chosen. These were crushed using an iron pestle and were subsequently pulverized using a tungsten carbide swing mill. Concentrations of rare earth elements (REEs) were obtained by lithium metaborate fusion with nitric digestion followed by inductively coupled plasma-mass spectrometry (ICP-MS) and ICP-emission spectrometry (ICP-ES).
at ACME Analytical Laboratories, Vancouver, Canada. The concentrations of REEs for the Nasirabad samples are given in Table 2. Samples from the Gugher were processed in Alchemex Co. \[12\], whereas samples from the Abadeh Tashk were processed by AMDEL Analytical Laboratories \[10\] (Table 2).

**Geochemistry**

The assessment of rare earth element (REE) geochemistry in ores offers insights into their genesis \[13\], with Mn ores being no exception, as has been described for numerous occurrences of modern and ancient ferromanganese deposits in the deep sea and terrestrial environments \[14\]. The REE data for the Nasirabad ore-bearing layers (n: 5) and nodules (n: 3) are listed in Table 1, and compared with published data for the Gugher manganese and ferromanganese deposit (n: 6), and Abadeh Tashk deposit (n: 3). All selected ore samples are characterized by relatively low REE abundance. The chondrite-normalized relative REE abundance patterns indicate a decrease of average ΣREE from Gugher ores (ΣREE= 38.79 ppm), to Abadeh Tashk samples (ΣREE= 33.09 ppm), Nasirabad ore-bearing layers (ΣREE= 19.7 ppm) and Nasirabad nodules (ΣREE= 8.94 ppm). In general, REE patterns exhibit distinct LREE enrichment relative to HREE and the LREE/HREE value decreases on average from Nasirabad ore-bearing layers (9.27), to the Abadeh Tashk (9.12), Nasirabad nodules (7.04) and Gugher ore samples (4.17), respectively. According to Ruhlin and Owen \[15\], the pronounced enrichment of the LREE relative to HREE can be attributed to the greater stability of HREE complexes in hydrothermal solutions.

In this study Cerium (Ce/Ce*) and Europium anomalies (Eu/Eu*) were calculated from: 

\[
\text{Ce/Ce*} = \text{Ce}_{\text{n}} / (\text{La}_{\text{n}} \times \text{Pr}_{\text{n}})^{1/2}, \quad \text{Eu/Eu*} = \text{Eu}_{\text{n}} / (\text{Sm}_{\text{n}} \times \text{Gd}_{\text{n}})^{1/2}
\]

\[16\], using chondrite-normalized abundances \[17\]. Taken as a whole, with the exception of the Nasirabad ore-bearing layers, ore samples from the selected areas have negative Ce anomalies (Fig. 2). Moreover, some have weak negative Eu anomalies (Eu/Eu*= 0.67 and 0.8 for the Nasirabad ore layers and nodules, respectively) whilst others have positive Eu anomalies (Gugher; average, Eu/Eu*= 1.20 and Abadeh Tashk (average, Eu/Eu*=2.79). It is important to note that the low REE concentration, positive Eu anomalies and weak or absent Ce anomalies are considered as common geochemical features of hydrothermal manganese and ferromanganese deposits \[18,19\].

In hydrothermal manganese and ferromanganese crusts \(\text{La}_n/\text{Nd}_n\) ratio is generally between 3.0–7.4 \[20\]. These ratios in the selected areas are analogous to those typical of hydrothermal crusts and decrease on average from the Nasirabad nodules (5.49) to Abadeh Tashk (4.14), Gugher (3.9) and the Nasirabad ore-bearing layers (3.62), respectively. The correlation diagrams indicate that there are strong positive correlations between the LREE and HREE, suggesting that the same mechanism was
### Table 2: The concentrations of REEs (ppm) and some major oxides (Wt. %) in the selected manganese deposits.

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<th>N3</th>
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<td>1.74</td>
<td>1.2</td>
<td>0.91</td>
<td>1.8</td>
</tr>
</tbody>
</table>

<sup>*[12], **[10].</sup>
responsible for REE uptake during the ore formation in Nasirabad, Gugher and Abadeh Tashk manganese and ferromanganese deposits\cite{20} (Fig. 3). Positive correlations were also observed between the $\Sigma$REE (ppm) and Fe$_2$O$_3$+MnO (wt. %) of selected samples from the Nasirabad and Gugher deposits, indicating progressive REE entrance into the Mn and Fe oxyhydroxides during the oxidation process (Fig. 3).

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According to Wright and Hosler \cite{21}, the Ce$_\text{anom}$ \cite{Ce_anom = Log (3 × Ce$_\text{anom}$/(2 × La$_\text{an}$+Ce$_\text{an}$))] can be used as a good index for the determination of oxic or anoxic nature of the water body of sedimentation. Ce$_\text{anom}$ $>$ -0.1 indicates anoxic condition during sedimentation, whereas Ce$_\text{anom}$ $<$ -0.1 represents oxidative conditions during deposition. The Ce$_\text{anom}$ values for the Gugher, Abadeh Tashk, and Nasirabad ore bearing layers and nodules are listed in Table 2. With the exception of the Nasirabad ore bearing layers (samples La4, La10 and La 1), all studied manganese deposits are characterized by Ce$_\text{anom}$ $<$ -0.1, reflecting oxidative conditions during the deposition of manganese ores.

Maynard \cite{22} has indicated that Al is insoluble in seawater at surface temperatures and can be used as a good indicator for the entrance of detrital materials into depositional basins. There is significant positive correlation between the $\Sigma$REE and Al$_2$O$_3$ contents of the Nasirabad ore-bearing layers, representing the effect of terrigenous materials during the formation of the Nasirabad manganese-bearing layers. Another indication of this may be seen in the Ce/La values. The Ce/La ratios increase from the Gugher deposit (average 0.46), to the Nasirabad nodules (average 0.90), Abadeh Tashk (average 1.06) and the Nasirabad ore-bearing layers (average 2.08). According to Dubinin and Volcov \cite{23}, increasing contribution from carbonaceous biogenic and terrigenous materials can elevate the Ce/La values. The geodynamic setting of Neyriz ophiolite has been discussed in detail by Shahabpor \cite{24} and Ghasemi and Talbot \cite{4}. The new geochemical data indicate the Neyriz was an intra-oceanic
island arc during the Late Triassic to Late Cretaceous time. Rezaei [1] and Zaravandi [25] pointed out that there are several lines of evidence, including Pb

Rezaei [1] and Zaravandi [25] pointed out that there are several lines of evidence, including Pb isotopes and major and trace inter-element relations, to show the contribution of mafic terrigenous materials (derived from the eruptions and/or erosion of Neyriz island arc) in the formation of Nasirabad ore sequences. Combining the REE results with $\frac{Al_2O_3}{(Al_2O_3 + Fe_2O_3)}$ ratios is useful to delineate the depositional environment of manganese ores [19]. In a $La_n/Ce_n$ versus $Al_2O_3/(Al_2O_3 + Fe_2O_3)$ discrimination plot [26], the average values of Nasirabad nodules and ore-bearing layers mainly plot in the pelagic field. However, the average values of Gugher in the Baft area plot in the field of spreading ridge proximal deposits (Fig. 5).

Figure 4: Strong linear correlation between the $Al_2O_3$ (wt. %) and $\Sigma$REE in the Nasirabad ore-bearing layers.
Figure 5: Plot of $\text{La}_n/\text{Ce}_n$ versus $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ for the Gugher in the Baft area, and the Nasirabad ore-bearing layers and nodules, modified after Murray\textsuperscript{[26]}. Normalizing values are from Evensen\textsuperscript{[17]}.

**Discussion and conclusion**

The ophiolitic rocks along the Zagros orogenic belt, a part of the Tethyan realm can be classified into two categories, the Naïen-Shahr Babak-Baft and Neyriz-Kermanshah ophiolite belts\textsuperscript{[4]}. These ophiolitic belts are characterized by widespread occurrence of manganese and ferromanganese deposits. It is important to note that, ophiolitic rocks hosting Mn and Fe bearing deposits are abundant along the Tethyan realm for example; Antalya complex, Turkey; northern Apennine ophiolitic complex, Italy; Troodos Massif, Cyprus; Semail nappe, Oman; Wazirestan complex, Pakistan. It is now generally understood that these deposits were commonly formed by hydrothermal processes similar to those of the present-day mid-oceanic spreading centers\textsuperscript{[1, 20, 27, 28]}.

According to Jach and Dudek\textsuperscript{[18]}, marine manganese deposits can be classified into three genetic types: Hydrothermal, Hydrogenous and diagenetic. However, these deposits can form by a combination of the aforementioned processes. Moreover, other parameters such as microbial processes and selective enrichment of bioessential elements and contribution of detrital materials in formation of deposits can give some special characteristics to manganese and ferromanganese deposits\textsuperscript{[1, 29]}. The Fe-Mn deposits from Gugher, Nasirabad and Abadeh Tashk (associated with the Baft and Neyriz ophiolitic rocks, respectively) are defined by low contents of REE, negative Ce anomalies (the Nasirabad ore bearing layers being the exception), LREE enrichment relative to HREE and $\text{La}_n/\text{Nd}_n$ values that resemble the
composition of hydrothermal manganese deposits formed by low temperature hydrothermal fluids [20, 30]. It has long been recognized that sediments precipitated from hydrothermal vent fluids yield pronounced positive Eu anomalies, with little or no negative Ce anomaly. The Gugher and Abadeh Tash samples have positive Eu anomalies (Eu/Eu*=1.2 and 2.79, respectively) as is commonly found in hydrothermal settings. In contrast, the Nasirabad samples show negative Eu anomalies (Eu/Eu* = 0.8 and 0.67 for the manganese nodules and layers, respectively). Such negative anomalies may result from high dilution of hydrothermal solutions with oceanic water due to the long distance between hydrothermal discharge and depositional environment in the Nasirabad area [31]. Moreover the lack of volcanics in the Nasirabad rock sequences provides further evidence for a remote source for the hydrothermal exhalations (distal hydrothermal source) [25, 32]. Another indication of this conclusion may be seen in the La*/Ce* versus Al2O3/(Al2O3 + Fe2O3) discrimination plat, where average values of Gugher samples plot in the proximal ridge district and Nasirabad samples plot in the pelagic district. The contribution of terrigenous materials, especially in the formation of Nasirabad manganese layers can be traced in the Ce/La values. The Nasirabad ore bearing layers are characterized by relatively high Ce/La ratio (2.08). Furthermore, such high Ce/La values and strong linear correlations between Al2O3 and REE (Fig. 4) provide an insight into the observed weak positive Ce anomaly in the Nasirabad ore-bearing layers (Fig. 2).

![Graph showing the comparison of hydrothermal deposits](image)

**Figure 6:** The compassion of Abadeh Tash, Gugher and Nasirabad manganese and ferromanganese deposits with Tokoro belt hydrothermal deposits [23], Peru basin Hydrogenous nodules [34] and Eymir deposit [20].
A comparison of REE patterns of Gugher, Aabadeh Tashk and Nasirabad manganese and ferromanganese deposits with Tokoro belt hydrothermal deposits [33], Peru basin Hydrogenous nodules [34] and Eymir deposit [20] is shown in Fig. 6. It seems that the REE pattern of manganese deposits associated with Zagros ophiolites are consistent with Tokoro belt and Eymir hydrothermal deposits.

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Session VII: REE Recycling Technologies
RECOVERY OF RARE EARTH METALS FROM END-OF-LIFE PERMANENT MAGNET SCRAP: AN OVERVIEW

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Abstract

NdFeB permanent magnets have different life cycles and wide range of sizes, from less than a gram to as big as 1000 - 2000 kg. Recycling of rare earth elements (REEs) contained in this type of magnets from the End-of-Life (EOL) products will play important and complementary role for the primary supply of the rare earth metals in the future. However, collection and recovery of the magnets from small consumer electronics imposes great social and technological challenges. This paper gives a board overview about the sources of NdFeB permanent magnets related to their applications, followed by summary of various available technologies to recovery the rare earth metals in the magnets, including physical separation, and metallurgical recovery. At present, no commercial operation has been identified for REE recycling from EoL NdFeB permanent magnets. Most of the processing methods are still under research and development stage.

Introduction

Neodymium-iron-boron (NdFeB) permanent magnets are the strongest and best available magnets in the market since their finding in 1984, and are highly efficient and suitable for lightweight mobile applications\textsuperscript{1}. They are widely in wind turbines, hybrid and electric vehicles (HEV and EV), household electrical appliances, computer hard disk drives (HDDs), and many small consumer electronic devices.

NdFeB permanent magnets have different life cycles, depending on the applications: from as short as 2-3 years in consumer electronics to 20-30 years in wind turbines. The size of the magnets range from less than a gram in small consumer electronics to over 1 kg in EV and HEVs, and can be as big as 1000 - 2000 kg in the generators of modern wind turbines. NdFeB magnet contains about 31-32% REEs, mainly Nd+Pr plus a few minor (but expensive) heavy REEs such as Dy, Tb and Ga, depending on the applications. Recycling of REEs in the NdFeB magnets from the End-of-Life (EOL) products will be complementary for the primary supply of the rare earth metals in the future. However, collection and recovery of the magnets from small consumer electronics imposes great social and technological challenges. Moreover, most EOL household electrical and electronic devices are currently shredded, the magnetic
content, mainly containing iron and neodymium, tend to end up in the generic ferrous metal stream, which is extremely diluted for economic REE recovery.

At present, no industrial operation and mature technologies have been identified for recycling the EOL NdFeB permanent magnets and the recovery of the associated REEs. It used to be simply cheaper to buy newly manufactured magnets than to reprocess the complex scrap material 2,3, especially for small-sized products where manually separating the magnet is challenging.

A few physical separation methods are recently reported for the treatment of the NdFeB permanent magnets from EOL products in computer hard disk drives (HDDs) and air conditioners, using mechanical shaking or hydrogen decrepitation 4-6. The reported processing methods are still under intensive development for future commercial application. The recovered magnet scrap still require metallurgical recovery and refining. From metallurgical aspects, there are various possibilities to recover the REEs in the NdFeB magnet scrap, including hydrometallurgical processing 7,8, and pyrometallurgical processing such as slag extraction 9,10, liquid metal extraction 11, molten salt extraction 12-14, chemical vapour transport 15,16. However, the majority of these techniques were developed to recover the REEs from pre-consumer (manufacturing) scrap or relatively clean and homogenous scrap with high REE concentration. The recovery of REEs from the complex post-consumer magnet scrap has not been well studied before.

This paper will give an overview on the sources of EOL permanent magnets and characteristics of their occurrence and applications, technical challenges and potential physical and metallurgical separation methods for the recovery of the magnets and the associated REEs. It is estimated that from 2030, the recycled REEs from the EOL permanent magnets will play a significant role in the total REE supply in the magnet sector, if efficient technologies are developed and used in practice 17.

Applications of NdFeB magnets and the source for recycling

NdFeB magnet production and market demand

Global annual REE production remains at the 120,000 tons level in recent years (counted as oxides - REOs). Approximately 26,000 tons REEs (counted as REO) are used as NbFeB permanent magnets which form the largest applications among all REEs both in tonnage and in market value 18,19, as is shown in Figure 1.

The great versatility of the REE magnet applications is also contributed by the fact that fine-tuning their chemical composition by adding some Dy, Tb, Nb, Co and Al can modify some of the physical and magnetic properties to suit wide application needs 20. Globally, about 76% of neodymium (Nd), 69% praseodymium (Pr) and gadolinium (Ga), and 100% dysprosium (Dy) have been used for permanent magnet production in recent years 21. In 2008, about 26,300 tons REEs including
Nd, Pr, Dy, Ga and Tb, counted as oxides, were used for magnet production.

Compared to other REEs, NdFeB permanent magnets and dysprosium are the most demanded materials, largely due to the fast growing green technologies for clean energy and transportation such as wind turbines and electric vehicles\textsuperscript{22}.

Figure 1: Market share of REE magnets in volume and monetary value (Created based on data of British Geological Survey\textsuperscript{18}).

REE permanent magnet contains about 31-32% REEs (mainly 21-31% (Nd+Pr), 0-10% Dy plus small amount of Ga and Tb)\textsuperscript{23}. Dy is critical for high temperature applications such as in EVs/HEVs. It is expected that the NdFeB permanent magnet market will continue to grow, and Figure 2 illustrates the global NdFeB permanent magnet production, and Table 1 lists the magnet production in year 2012 and prediction for year 2015. As is clearly illustrated in Figure 2 and Table 1, Japan and China have been the two main REE magnet producing countries, and in recent years China is by far the dominant producing country.

\begin{table}
\centering
\begin{tabular}{lcc}
\hline
Production by country/region & 2012 & 2015 prediction \\
\hline
China & 50 & 65 \\
Japan & 10 & 8 \\
Europe & 1 & 1 \\
USA & 0 & 2 \\
All others & 2 & 2 \\
\hline
Total REE magnet & 63 & 78 \\
Total REE in magnet (31%), estimates & 19.5 & 24.2 \\
\hline
\end{tabular}
\caption{Production of NdFeB permanent magnets (x 1000 metric tons)\textsuperscript{24}}
\end{table}

**Applications of NdFeB magnets**

Figure 3 shows the relative REE magnet applications, predicted for the year end 2012 by Shaw and Constantinides\textsuperscript{19}. Computer hard disc drives (HDD) and CD/DVDs used to be the number 1
applications of the REE permanent magnets, and as is seen, motors and generators are becoming the most important applications in recent years.

(a) Total global NdFeB magnet production and prediction: 2005 – 2020

(b) Total global REE demands in the permanent magnets

Figure 2: Global production of NdFeB permanent magnets and the demand for the REEs

According to Heli Magnetic Technology Co., Ltd. [http://www.helimagnet.com], the proportion of NdFeB magnets used in different applications are estimated as follows:

- Over 40% for the electric bike motors, industrial motors, car motors and other electrical products
- 30% for microphones and sound amplification equipment
- 10% for mobile phones, MP3, CD, DVD, headphones, and other consumer electronics
- 8% for household electrical appliances
- 5% photocopiers and other office equipment
- and 7% for the applications in other areas.

Table 2 (next page) lists the main applications of NdFeB magnets and the relative market size and the total estimated annual demand for 2012/2013. The total estimated demand for the REE magnets is about 63,000 tons, excluding the household appliances.

**Recycling potential of NdFeB permanent magnets**

According to the estimations of Du and Gradael\textsuperscript{26}, global in-use stocks for four rare earth elements in NdFeB permanent magnets neodymium (Nd), praseodymium (Pr), terbium (Tb), and dysprosium (Dy), amount to a total of 97.0 kt: 62.6 kt Nd, 15.7 kt Pr, 15.7 kt Dy, and 3.1 kt Tb. These stocks, if efficiently recycled, could provide a valuable supplement to geological stocks as they are almost four times the 2007 annual extraction rate of the individual elements. Different applications of the four REEs as permanent magnets estimated by Du and Gradael\textsuperscript{26} are listed in Table 3.

<table>
<thead>
<tr>
<th>Stocks (kt)</th>
<th>Nd</th>
<th>Pr</th>
<th>Dy</th>
<th>Tb</th>
<th>Total</th>
<th>Share (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computers</td>
<td>21.2</td>
<td>5.3</td>
<td>5.3</td>
<td>1.1</td>
<td>32.8</td>
<td>33.8</td>
</tr>
<tr>
<td>Audio systems</td>
<td>15.1</td>
<td>3.8</td>
<td>3.8</td>
<td>0.8</td>
<td>23.4</td>
<td>24.1</td>
</tr>
<tr>
<td>Wind turbines</td>
<td>10.1</td>
<td>2.5</td>
<td>2.5</td>
<td>0.5</td>
<td>15.7</td>
<td>16.2</td>
</tr>
<tr>
<td>Automobiles</td>
<td>9.8</td>
<td>2.5</td>
<td>2.5</td>
<td>0.5</td>
<td>15.2</td>
<td>15.7</td>
</tr>
<tr>
<td>Household</td>
<td>3.3</td>
<td>0.8</td>
<td>0.8</td>
<td>0.2</td>
<td>5.1</td>
<td>5.3</td>
</tr>
<tr>
<td>MRI</td>
<td>3.0</td>
<td>0.8</td>
<td>0.8</td>
<td>0.2</td>
<td>4.7</td>
<td>4.8</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>62.6</td>
<td>15.7</td>
<td>15.7</td>
<td>3.1</td>
<td>97.0</td>
<td>~100</td>
</tr>
</tbody>
</table>

Rademarker et al.\textsuperscript{17} estimated the recycling potential of NdFeB permanent magnets for 3 application sectors by considering the manufacturing and life span of the applications: computer hard disc drives, wind turbines and automotive industry. The results show that for some time to come, waste flows from permanent magnets will remain small relative to the rapidly growing global REE demand. Policymakers therefore need to be aware that during the next decade recycling is unlikely to substantially contribute to global REE supply. In the long term, waste flows will increase sharply and will meet a substantial part of the total demand. Figure 4 shows the recycling potential of Nd and Dy for the 3 studied application sectors.
### Table 2: Applications of NdFeB permanent magnets and the estimated annual demand (2012/2013)

<table>
<thead>
<tr>
<th>Sectors</th>
<th>Product</th>
<th>Concrete use</th>
<th>Mass/ unit</th>
<th>Total use (ton)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consumer electronics</td>
<td>Computer HDDs, CDs, DVDs Home electronics &amp; electrical appliances*</td>
<td>VCM, SP motors Small electric motors and speakers</td>
<td>10-20 grams</td>
<td>14,200 (22.5%)</td>
<td>Based on references $^{19,25}$. Speakers in sound system, mobile phones and music players; washing machines, refrigerators and air conditioners etc.</td>
</tr>
<tr>
<td>Wind turbines</td>
<td>Generation IV (only)</td>
<td>Generators</td>
<td>400 kg/MW</td>
<td>16,000 (25.4%)</td>
<td>200 kg/MW for hybrid drive, 600 kg/MW for direct drive$^{25}$.</td>
</tr>
<tr>
<td>Vehicles</td>
<td>Conventional automobiles</td>
<td>Small motors (40) and sensors (20)</td>
<td>250 grams</td>
<td>20,900 (33.2%)</td>
<td>Based on Shaw and Constantinides $^{19}$. Cars at different ages contain 220-560 g REE magnets/car $^{27}$. 83.5 million new vehicles in 2013 [247wallst.com].</td>
</tr>
<tr>
<td></td>
<td>HEVs, PEHVs and EVs</td>
<td>Electric motors</td>
<td>1.25 kg*</td>
<td>2,200 (3.5%)</td>
<td>1.776,543 sales in 2013 [EVsRoll.com]</td>
</tr>
<tr>
<td></td>
<td>Electrical bikes (EB)</td>
<td>Electric motors</td>
<td>300-350 grams</td>
<td>9,700 (15.4%)</td>
<td>30 million/year in 2012$^{25}$.</td>
</tr>
<tr>
<td>Total (incomplete)</td>
<td></td>
<td></td>
<td></td>
<td>63,000 (100%)</td>
<td>This figure does not include the magnet consumption from major household appliances.</td>
</tr>
</tbody>
</table>

* Large household appliances include refrigerators (containing 40–60 g NdFeB magnets per unit), washing machines (80–180 g NdFeB/unit), and air conditioners (60–400 g NdFeB/unit)$^{27}$. Suppose an average REE magnet of 50-100 g/unit and a global sales of 200 million unit per year: total magnet consumption will be 10,000 – 20,000 ton/year for this sector.

* *This figure does not include the magnets in the small motors and sensors like in the conventional cars$^{25}$.

The main application sectors are conventional automotive (33.2%), wind turbines (25.4%), computer HDDs/CDs/DVDs (22.5%), E-bikes (15.4%), and EVs/HEVs (3.5%), according to this study. It can be seen that this differs from the estimations by Constantinides$^{25}$ and Shaw and Constantinides$^{19}$, however, the classifications of the application areas are different. When recycling is concerned, the wide range of life span of different products need to be carefully considered.

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Figure 4: Recycling potential of Nd and Dy from EOL permanent magnets (2011 – 2030 prediction) adapted from Rademarker et al.\textsuperscript{17}

Rademarker et al.\textsuperscript{17} emphasized that for consumer products, one of the recycling challenges is the physical dismantling and up-concentration of small NdFeB magnets in the diversified scrap. REE magnets in wind turbines and EV/HEV vehicles are more easily dismantled and physically concentrated, and even reuse is possible after refurbishing. In general, efficient metallurgical separation and refining processes remain the main challenges. Future REE recycling efforts should, therefore, focus on the development of recycling technology and build-up of the infrastructure. It is estimated that about five to ten years is required to set up a recycling practice.

**Physical separation technologies**

**Destination of permanent magnets in different EOL products**

Except for generators and motors in wind turbines and EV/HEVs, the REE permanent magnets are not pre-dismantled, due to their relatively small size, from their attached EOL products in computer HDDs and other home electronics such as mobile phones, music players and speakers in the sound systems. The EOL electronic products (e-waste) are generally shredded as a whole after removal of the hazardous components/materials. Because of the strong permanent magnetism, the small magnets will stick to ferrous scrap (steel) after shredding and physical separation using such as magnetic separators, or to a much smaller extent trapped to the non-ferrous scrap if the magnets are not liberated and still stuck to the non-
ferrous components. At present, almost all small permanent magnets used in consumer electronics (at relatively low collection rate), after collection and shredding operation, are lost into ferrous scrap and reported into slag during metallurgical smelting or refining processes of the major metals.

For the generators in wind turbines the REE permanent magnets, after reaching their end of first life, can still be manually dismantled and reused or recovered for the REEs much more easily due to their large size (250 – 600 kg/MW power). For the conventional automobiles, there are around 40 magnets in small motors and actuators and 20 sensors in a typical passenger car, and on average there are about 250 grams of NdFeB magnets and 10-20 grams SmCo magnets\(^{19}\). These small permanent magnets are not pre-dismantled before car shredding in the present industrial practice, and they are simply lost to the ferrous scrap similar to the magnets in the consumer electronics. The REE permanent magnets in the electric motors of EVs and HEVs are relatively larger than in normal cars (on average 1.25 kg, see Table 2) but still difficult to dismantle manually, and thus are more likely lost in the ferrous scrap.

Depending on the market value, pre-dismantling of the REE magnet-containing components in major consumer products should be an option for further mechanical and metallurgical recovery in the future. Therefore, there is an increasingly great demand for the design of magnet for dismantling in the consumer products.

**Analysis of REE magnets in the shredder material streams**

*Conventional shredding for End-of-Life Vehicles (ELVs) and household appliances*

As is discussed earlier, most of the permanent magnets nowadays go to shredders together with the bonded EOL products. A recent study by Bandara et al.\(^{27}\) gives a good overview about the destinations and concentrations of the permanent magnets and the associated REEs. Their study for shredding ELVs and household appliances indicates that the ferrous scrap of the shredder products attracts most of the magnetic materials and contains about 130 – 290 grams of Nd/ton (ppm). This concentration is even much lower than the REEs content in some mine tailings of up to 1000 – 1500 ppm. Without pre-concentration and novel technologies, the low REE content in the scrap is very difficult to recover. Thus, technologies for pre-shredder separation are needed for any feasible metallurgical recovery.

**Separated shredding of pre-dismantled HDDs and air conditioners**

*Shredding and physical upgrading of pre-dismantled computer HDDs*

Pre-dismantling of computer hard disk drives have been reported by some companies mainly for data security reasons, although this is not a standard practice. The dismantled hard disk drives are shredded and normally the ferrous and non-ferrous scrap as well as the printed circuit boards (PCBs) are recovered. In most cases, the REE magnets particles after shredding are not recovered although the REE concentration is much higher than those in the shredder...
ferrous products from the whole EOL product (e.g. computers).

In the Netherlands, Van Gansewinkel Group operates a small shredder for HDD shredding (data destruction). TU Delft has recently developed a REE recover process from the magnet concentrated HDD shredder residues\textsuperscript{10,28}. The separately collected magnet residues go through a thermal demagnetization process followed by grinding and screening. The highly concentrated magnet particles (containing up to 25% Nd) separated from the ductile metal pieces can go through either hydrometallurgical extraction or first processed with slag extraction followed by REE leaching. The REE product of fluoride or oxide can be prepared for final RE metal production. Figure 5 illustrates the developed processing flowsheet. The magnet concentrate particles of less than 1 mm size range represent 63% of the total collected shredder residue, and a total of 95% recovery rate has been achieved for all the REEs in the collected residues through physical processing.

Figure 5: Processing flowsheet for the REE recovery from EOL HDDs at TU Delft.

**Hydrogen decrepitation of pre-dismantled computer HDDs**

University of Birmingham has developed a hydrogen processing method to selectively convert sintered NdFeB magnet into hydride fine particles at room temperature and atmospheric pressure, or high temperature and pressure (170°C and 7 bar) for Ni alloy coated magnets\textsuperscript{4,5}. The formed Nd hydride has a 5% volume expansion which makes the Nd hydrides into fine demagnetized powders. The fine powders can be easily separated from the main structure of the HDDs. The Nd hydrides can be converted to REE metal (alloy) at elevated temperatures by releasing hydrogen (a desorption process). If the source of the magnets is very clean, the REE magnet powder could be re-sued directly for magnet manufacturing. If the source of magnets is contaminated, the magnet powder could be re-processed through chemical and metallurgical technologies back to pure REE or their alloys. Further research is going on to treat the low concentration EOL magnet scrap in a recently EU funded project “EREAN” (European Rare Earth Magnet Recycling Network: [http://erean.eu](http://erean.eu)).
Mechanical separation of magnets from HDDs and air conditioners

Hitachi Group developed a mechanical dismantling and separation technique for NdFeB magnets in HDDs and air conditioners, using a rotational dram. Through vibration and impact by tumbling, the screws fixing the HDD casing become loose, and the magnets can be separated out of the casing in about 30 minutes. The apparatus can process 100 HDDs per batch and 200 HDDs per hour, much faster than manual dismantling of 12 units per hour. Mitsubishi and Mitsubishi Materials have also developed similar technology to recovery the NdFeB magnets from the compressors in air conditioners. After cutting off the casing, the rotors in the compressor can be removed and treated by either non-thermal demagnetization (Hitachi) or thermal demagnetization at 400 – 500°C (Mitsubishi). Hitachi may use the similar rotating drum for HDDs disintegration to loosen the magnets from the air conditioner, and Mitsubishi uses other equipment (e.g. drills). Furthermore, Mitsubishi Materials is also trying to separate the NdFeB magnets from direct drive (DD) motors in washing machines through thermal demagnetization and removing the resin bounding.

Metallurgical extraction and separation

There have been many studies for the recovery of Nd and other associated REEs (Pr, Dy, Tb) using various types of metallurgical processes: hydrometallurgical, pyrometallurgical and electrochemical, or their combinations. However, most of these studies have focused on the highly concentrated and relatively clean waste magnets of manufacturing scrap or production waste: the new solid scrap and cutting sludge “swarf” which accounts for 20-30% of the starting alloy for manufacturing the magnets. The solid scrap is normally re-melted (after coating removal) within the magnet manufacturing plant for direct re-use. However, the swarf requires chemical or metallurgical separation and refining mostly through hydrometallurgical leaching route to produce rare earth fluorides or oxides as raw materials for conventional metal production (molten salt electrolysis or metallothermic reduction). Recently published two comprehensive reviews on rare earths recycling by Binnemans et al. and Tanaka et al. are good sources of reference. Binnemans et al. gave a good comparison for different metallurgical methods as is partially listed in Table 4 below. It should be noted that except for direct melting of the relative clean magnet scrap, all the listed methods convert the REE magnet in the scrap or waste into REE halides or oxides, which need to be reduced to RE metal or alloys through either molten salt electrolysis or metallothermic reduction, like the treatment of “swarf”.

Table 4: Comparison of different metallurgical methods for REE recovery from NdFeB magnet scrap, extracted from Binnemans et al.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrometallurgical</td>
<td>• Generally applicable to all types of magnet compositions</td>
<td>• Many process steps required before obtaining new magnets</td>
</tr>
<tr>
<td></td>
<td>• Applicable to non-oxidized and oxidized alloys</td>
<td>• Consumption of large amount of chemicals</td>
</tr>
</tbody>
</table>
### Methods

**Pyrometallurgical:**
- Generally applicable to all types of magnet compositions
- No generation of waste water and effluents
- Fewer processing steps vs. hydrometallurgical methods
- Direct melting for obtaining master alloys
- Liquid metal extraction allows for obtaining REEs in metallic state

**Pyrometallurgical: Liquid-phase processing**
- Generally applicable to all types of magnet compositions
- No generation of waste water and effluents
- Fewer processing steps vs. hydrometallurgical methods
- Direct melting for obtaining master alloys
- Liquid metal extraction allows for obtaining REEs in metallic state

**Pyrometallurgical: gas-phase extraction**
- Generally applicable to all types of magnet compositions
- Applicable to non-oxidized and oxidized alloys
- No generation of waste water and effluents

- Generation of large amount of waste water and effluents
- High energy input required
- Direct melting and liquid metal extraction cannot be applied to oxidized magnets
- Glass slag method generate large amounts of solid waste, REE-bearing slag still requires further hydrometallurgical processing.
- Consumption of large amount of chlorine gas
- Aluminum chloride is very corrosive

### For the small magnets used in the EOL consumer products, little recycling efforts could be identified and it was commonly thought that less than 1% of the EOL REEs (including REE magnets) has been recycled, mainly due to the their small size, tight bonds with the product and the multiple type mixture of different magnets (ferrites, SmCo and NdFeB). It is one of the main objectives of this paper to identify feasible metallurgical recovery techniques for extraction of the small sized magnets in their bound EOL products. Although the past research has focused mainly on the manufacturing scrap and residue (swarf) recycling, the developed methods could be adapted to the EOL magnet scrap for REE recovery.

As is discussed in previously, the magnet or REE concentration would be too low for metallurgical recovery if the EOL products (automobiles, home electrical appliances and consumer electronics) are directly shredded. Pre-dismantling and up-concentration through physical processing are critical for a viable chemical or metallurgical extraction. Recovery of the minor amount of REEs from the magnet scrap is both technically and economically very challenging. Allocating the REEs originated from the magnet scrap in the by-product or waste streams of smelting processes for main metals is a potential possibility, including slags, flue dust, solid leach residues and waste solutions. Therefore, a total materials recovery from EOL products (containing REE magnets) would be the direction for future research and development, in parallel with magnet pre-dismantling approach.

### Hydrometallurgical methods

The key steps for hydrometallurgical route are leaching of the magnet scrap or waste, followed by precipitation of the REE salts or compounds and further conversion to REE fluorides or oxides, quite often with REE separation or up-concentration in between. The leaching can be performed in three different ways: (1) complete leaching (with or without roasting, (2) roasting – selective
REE leaching, and (3) selective conversion of REEs. Furthermore, conversion of REEs in the magnet scrap into REE compound precipitates based on solubility of REE salt at different temperatures or under hydrothermal conditions is also an option. Table 5 lists the major hydrometallurgical methods reported in the literature.

The challenges for the hydrometallurgical leaching process to recover the RREs in the EOL permanent magnets, in particular the REE dilute waste streams, are the selective dissolution, up-concentration and separation of REE species from the major species, and total recovery of all major metals at the same time. Therefore, new separation technologies such as novel solvent extractants, ionic liquid, ion exchange resin or the alike, are strongly needed to extract REE species from low concentration leaching solutions. Alternatively, anodic dissolution of NdFeB permanent magnet scrap is a potential option to dissolve REE species electrochemically\textsuperscript{23}, separating non-REEs in the scrap into anode slimes or precipitated onto the cathode, through accurate control of electrode and cell potentials and current density on the electrodes, as well as proper selection of electrolyte.

**Pyrometallurgical methods**

The main purpose of high temperature processing of NdFeB magnet scrap is to selectively convert REEs in the magnet into another phase which separate the main non-REE components. The separated REEs in another phase would be much more concentrated and can be used for RE metal production through molten salt electrolysis or metallothermic reduction. The identified pyrometallurgical extraction methods can be divided into the following groups: (1) selective chlorination, (2) liquid metal extraction, (3) molten salt extraction, (4) molten slag extraction, and (5) electrochemical processing.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Main features</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Leaching or conversion</strong></td>
<td>With H\textsubscript{2}SO\textsubscript{4} leaching at room temperature, all components in NdFeB magnet will be dissolved. Nd can be precipitated as double slat which can be converted to NdF\textsubscript{3} or Nd\textsubscript{2}O\textsubscript{3}. Large amount of Fe dissolved in the solution needs to be properly disposed (e.g. jarosite precipitation). Roasting at 500°C for sintered scrap and at 700°C for bonded scrap followed by H\textsubscript{2}SO\textsubscript{4} (2 mole/l) leaching at 50°C for 2 h and double salt precipitation. Nd yield was over 99.9%.</td>
<td>Layman and Palmer\textsuperscript{8}, Abrahami et al.\textsuperscript{28} Yoon et al.\textsuperscript{34}</td>
</tr>
<tr>
<td>Selective leaching (with roasting)</td>
<td>Roasting in air at 700°C followed by H₂SO₄ (4 mole/l) at 70°C for 3 hours with pulp density of 100 kg/m³, with 70% Nd recovery.</td>
<td>Lee et al.³⁵</td>
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<tr>
<td></td>
<td>Roasting at 900°C for 6 h followed with HCl (0.02 mole/l) leaching at 180°C for 2 h. More than 99% REE and less than 5% Fe recovery.</td>
<td>Koyama et al.³⁶, Koyama and Tanaka³⁷</td>
</tr>
<tr>
<td>Fractional crystallization (Nd sulfate conversion)</td>
<td>A simultaneous dissolution and precipitation process by making use of the decreased solubility of Nd₂(SO₄)₃ at elevated temperatures. Adding ethanol to H₂SO₄ facilitates the precipitation. With 97.1% Nd yield and 96.8% purity of Nd sulfate hydrate.</td>
<td>Wei et al.³⁸, Sato et al.³⁹</td>
</tr>
<tr>
<td>Hydrothermal conversion</td>
<td>Using mixture of HCl (3 mole/l) and oxalic acid (0.2 mole/l) to recover Nd as oxalate. Operating condition: 110 °C and 6 h. Over 99% of Nd in the magnet recovered as solid precipitate of Nd₂(C₂O₄)₃ with of 99.8 purity %.</td>
<td>Itakula et al.⁷</td>
</tr>
</tbody>
</table>

### REE separation & concentration

<table>
<thead>
<tr>
<th>Solvent extraction</th>
<th>Conventional process with many different organic extractants for REE separation in primary REEs production. This technique would be applicable to the REE recycling in the hydrometallurgical route after leaching for REE separation from non-REEs (may require necessary modifications) and separation of individual REEs.</th>
<th>Xie et al.⁴⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic liquid extraction</td>
<td>Potential alternative to organic solvent extractants due to low vapor pressure and stability. Ionic-liquid based liquid membrane with permeability to REE ions.</td>
<td>Baba et al.⁴¹, Binnemans⁴²</td>
</tr>
</tbody>
</table>

### Selective chlorination

For selective chlorination of REEs in the magnet, various chlorination agents have been investigated: using metal halides such as MgCl₂ to convert the REEs into molten NdCl₃ and DyCl₃ at 1000°C¹²,¹³, using FeCl₂ at 800°C¹⁶, using NH₄Cl at much lower temperature of 300°C¹⁵, or using Cl₂ gas and AlCl₃ (the so called chemical vapor transport process)⁴⁴. In most of these cases, the RECl₃ (NdCl₃ and DyCl₃) were distilled at elevated temperatures to separate from Fe-based residue. For all chlorination approach, selectivity and the reaction rate would be key issues, in particular when treating highly contaminated and partially oxidized magnet scrap.

### Liquid metal extraction

The Ames Laboratory has developed a liquid metal extraction process to recycle REEs from NdFeB and other alloys⁴⁵, and later studied further by other researchers using Mg as extractant ¹¹, ⁴⁶, ⁴⁷. However, this process is very slow (24 – 72 hours) and cannot be applied to (partly) oxidized NdFeB scrap.
**Molten salt extraction**

Okabe and Shirayama\(^{12,13}\) used molten MgCl\(_2\) to selectively dissolve Nd and Dy from the NdFeB magnet scrap at 1000°C, and about 90% of REEs can be extracted in about 12 hours. The obtained molten mixture of Mg – MgCl\(_2\) – NdCl\(_3\) – DyCl\(_3\) goes through a distillation process to remove Mg and MgCl\(_2\) as vapor, and the separated REE chloride can be used for RE metal production. Very recently, Hua et al.\(^{14}\) developed an integrated process using molten chloride slat (MgCl\(_2\) – KCl) extraction to selectively dissolve Nd and other REEs in the magnet scrap at temperature of 700 – 1000°C. An REE recovery of approximately 90% has been obtained, and the formed NdCl\(_3\) in MgCl\(_2\) – KCl salt can be subsequently electrolyzed to produce directly Mg-Nd alloy. Tanaka et al.\(^{6,48}\) proposed a process by using molten fluoride to remove the oxidized rare earth in the NdFeB magnet scrap. In this process, the molten fluoride reacts with the rare earth oxides and the formed REO – fluoride mixture is used in molten salt electrolysis for RE metal production. The un-oxidized NdFeB scrap remain unreacted and is thus cleaned as master alloy for magnet preparation again. It should be noted that molten chloride salts can be used for treatment of un-oxidized magnet scrap only, while molten fluoride salts are suitable for the treatment of oxidized magnet scrap only.

**Molten slag extraction**

Two slag treatment methods are reported in the literature. In the glass slag method, the REE alloy is brought into contact with a molten B\(_2\)O\(_3\) that is able to selectively oxidize and dissolve the rare earths from the alloys to form Nd\(_2\)O\(_3\)-B\(_2\)O\(_3\) slag\(^9\). The slag can be subsequently leached with acid to extract Nd precipitate such as Nd(OH)\(_3\), but with relatively low Nd recovery\(^{49}\).

The second slag method is the use of CaO-SiO\(_2\)-Al\(_2\)O\(_3\) or CaO-CaF\(_2\) fluxes to extract the REEs in the complex magnet scrap at about 1500°C\(^{10}\). This method is very effective for the EOL magnet scrap such as HDD shredder residues with more than 99% REE recovery. It can separate completely the REEs in the magnet from the ferrous materials in the NdFeB magnet and the mixed scrap. The REE-rich slag can be used for hydrometallurgical extraction, and the separated iron-rich alloy can be a good source of raw materials for steelmaking. The advantages of molten slag extraction is its capability of effective separation of REEs and iron, and the recovery of both fractions at the same time.

According to Tanaka et al.\(^6\), Yamamoto’s group reported an in-plant waste (sludge) separation process where the magnet waste separates into liquid iron and solid rare-earth oxide phases at 1550°C under argon atmosphere with low O\(_2\) partial pressure without any flux additions. It was found that all of the REEs in the magnet waste were converted to the oxide phase, and the formed REOs can be converted to RE metal through conventional technologies.

**Electrochemical process**

The electrochemical processes can be applied to the metallic magnet scrap based on electro-refining principles in the molten salt\(^{6,50,51}\). In a molten salt electro-refining cell, the impure REE magnet scrap used as starting anode can be selectively dissolved for rare earth elements
(Nd and/or Dy) in a molten chloride or fluoride electrolyte, and on the cathode only REEs are preferably deposited forming Nd-based alloys. In the cell a rare earth – iron group metal alloy is used as bipolar electrode (diaphragm).

As can be seen from the above discussion, most of the pyrometallurgical methods are applicable to only highly concentrated magnet scrap (production waste: off-specs and swarf), and adaptation is required to treat the dilute EOL magnet scrap. Slag extraction may be a very promising method to separate and up-concentrate the REEs in the low concentration magnet-bearing scrap such as shredder residues, however, subsequent hydrometallurgical extraction such as REE leaching is needed.

**Concluding remarks**

This paper addresses the recycling potential of NdFeB permanent magnets and the identified physical and metallurgical separation and recovery technologies. It is indicated that the annual consumption and demand of the REE magnets are continuously increasing, and the recycling of the REEs in the EOL permanent magnets will be complementary to the supply shortage in the long run. REE recovery from the manufacturing scrap and waste (swarf) of the NdFeB magnets is already a good industrial practice with available technologies.

However, recycling and recovery of REEs (Nd, Pr, Dy, Tb) from EOL magnets are challenging due to their relative small size used in consumer electrical and electronics, as well as in the conventional automotive industry. Shredding without pre-dismantling of the EOL consumer products will pose great difficulties for up-concentration of the permanent magnets. Development of advanced and low cost of pre-disassembling technologies or equipment will be crucial for the metallurgical recovery of REEs. This has been demonstrated by the developments for computer hard disk drives and air conditioners by Hitachi and Mitsubishi, Birmingham University, Delft University of Technology, and active European initiatives such as EREAN ([http://erean.eu](http://erean.eu)) and REEcover consortia and other global government supports in Japan and USA reported in recent years.

There are many different types of metallurgical recovery methods identified from the literature, however, most of them have been studied for relatively clean and highly concentrated new or manufacturing magnet scrap and waste. Adaptation of these technologies to the dilute and complex EOL magnet scrap is highly needed. At the same time, recovery of the major metals and materials in the dilute magnet waste stream (e.g. shredder products) is an important factor for the total success of the permanent magnet and REE recycling. It is believed that no single metallurgical process can be successful for the efficient recovery of the REEs from their EOL secondary resource, and a combination of hydrometallurgical, pyrometallurgical and/or electro-chemical technologies will be the future path for the most promising.
solution. It is expected that through the globally increasing efforts (Europe, Japan, USA, China) for the research and development, establishment of technologically and economically feasible REE magnet recycling industry could be realized in the near future, if the NdFeB permanent magnet market continue to develop.

References
20. Sagawa M., Fujimura S., Yamamoto H., Matsuura Y. and Hiraga K., Permanent magnet materials based on
LEACHING OF RARE EARTH ELEMENTS: PAST AND PRESENT

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Abstract

The recycling of Rare Earth Elements (REE) from mine tailings and REE containing End-of-Life (EoL) scrap, the two main secondary resources, offers great opportunities to secure REE supply in Europe. The relatively low concentration of REE in mine tailings (1000-1500 ppm) and the variety in contaminants in the EoL scrap have made the extraction of REE from these resources very challenging. This paper provides a review of the past and present technologies for REE leaching used in primary REE production and in REE recycling, as an important part of hydrometallurgical REE processing. Detailed studies of existing processes are essential to properly understand and resolve the difficulties in REE recycling from these secondary resources. The known processes range from acid leaching with $\text{H}_2\text{SO}_4$, $\text{HCl}$ or $\text{HNO}_3$ for primary ores, to leaching with NaCl or $(\text{NH}_4)_2\text{SO}_4$ of ion adsorbed clays and combined base and acid leaching for EoL lamp phosphors. A comprehensive understanding of these processes is the key to applying them to REE recycling from secondary resources.

I. Introduction

The rare earth elements (REE) are a group of 17 chemically similar elements consisting of the lanthanides, Y and Sc. Their unique physical and chemical properties have made them essential in state-of-the-art equipment (e.g. magnets, catalysts, batteries). A potential supply risk of REE, environmental concerns and economic benefits promote research on processing of secondary materials, such as mine tailings or electronic waste, in the EU. Although significant investigations on REE extraction from secondary resources have been carried out and a variety of technologies have been developed or proposed, most of them are still in the stage of research or only suitable for some specific secondary resources. The REE extraction efficiency and selectivity, together with the cost and engineering during process design, still require substantial optimisation before further commercialisation. At the same time, the understanding of interactions between REE minerals in a low concentration and the leaching media, as well as the behaviour of selective leaching of different REE phases in magnet scraps, is still not sufficient. In order to have a better view on the state-of-the-art and to improve engineering possibilities of REE extraction from secondary resources, a review of the most prevailed leaching technologies that are currently in use in REE production is needed.
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Process</th>
<th>REE yield</th>
<th>Remarks</th>
<th>Status</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| Bastnaesite | 1) HCl leach to remove non REE carbonate  
2) Calcination of residue to form REO | 85-90%   | The oldest way to process bastnaesite concentrates                                      | outdated | [3]  |
|         | Digestion with HNO₃ or H₂SO₄                                             | 98%       | Acid choice depends on further processing: solvent extraction → HNO₃ precipitation → H₂SO₄ | outdated | [3]  |
|         | 1) Roast at 620°C to drive of CO₂  
2) 30% HCl leach                                                               | --        | Ce³⁺ oxidises to Ce⁴⁺ during roasting → will not leach REE fluorides will not leach, residue is marketable | outdated | [3]  |
|         | 1) Alkaline conversion REF₃ → RE(OH)₃  
2) HCl leach                                                                  | --        | Process can be preceded with HCl leach to extract REE carbonates before alkaline conversion | In use   | [3]  |
|         | 1) Sulphuric acid roast  
2) NaCl solution leach  
3) Precipitation as Na double sulphates                                      | --        | Precipitates are converted to chlorides for further purification with solvent extraction | In use   | [3]  |
| Monazite  | Digestion in hot H₂SO₄                                                  | --        | Process conditions determine what is leached: only LREE or LREE+HREE+Th  
Yields no pure product                                                                 | outdated | [3]  |
|         | 1) Digestion in hot 60-70% NaOH  
2) Washing residue with hot water  
3) Leach with mineral acid of choice                                         | 98%       | Ce cannot be leached if Mn is present  
Th is leached together with REE  
Na₃PO₄ is marketable by-product                                                   | In use   | [3-4]|
|         | 1) Heat under reducing and sulphidizing atmosphere with CaCl₂ and CaCO₃  
2) Leach with 3% HCl                                                           | 89%       | Requires no fine grinding  
Th does not leach, remains in residue as ThO₂  
No Mn problem                                                                       | In use   | [5]  |
| Ion clay | Salt leach with (NH₄)₂SO₄                                                | 80-90%    | Targets physisorbed REE through cation exchange                           | In use   | [7]  |
|         | Leach with seawater                                                      | 40%       | Inefficient but cheap process                                             | R&D     | [8]  |
|         | Acid leach with strong acid (pH<1)                                       | ALL       | Dissolves entire clay, incurs significant additional costs                | Not used | [7]  |
II. Leaching technologies in primary REE production

The main REE minerals used in primary REE production are bastnaesite and monazite. Next to these, ion adsorbed clays are lower grade resources, which due to their easy processing are becoming more popular as a primary resource. Table 1 offers a concise overview of the leaching technologies, both past and present, used in primary REE production.

Bastnaesite

Bastnaesite is a rare earth fluorocarbonate mineral\(^1\), RE(CO\(_3\))F, which primarily contains light rare earth elements. After physical upgrading, bastnaesite ore concentrates contain between 40 to 60% REE\(^2\).

One of the main concerns in past bastnaesite processing technologies (see table 1) was the inability to extract the REE fluorides. It has been successfully resolved in the current day technologies in two different ways: pre/post-treatment with alkaline or sulphuric acid roasting. The alkaline treatment, developed by Kruesi and Duker of Molycop\(^3\), is a three step process, using the following reactions:

\[
\begin{align*}
REF_3 - RE_2(CO_3)_3 + 9HCl & \rightarrow REF_3 + 2RECl_3 + 3HCl + 3H_2O + 3CO_2 \\
REF_3 + 3NaOH & \rightarrow RE(OH)_3 + 3NaF \\
RE(OH)_3 + 3HCl & \rightarrow RECl_3 + 3H_2O
\end{align*}
\]

(1) (2) (3)

Step I - a mild HCl solution to extract the REE carbonate, step II - reaction with NaOH at 96°C to convert the REE fluorides to hydroxides, which are then dissolved by leaching with HCl in step III. Alternative processes exist, which skip the first leaching step and instead the bastnaesite is first treated with alkaline and then leached with HCl\(^3\).

Sulphuric acid roasting is the other main process currently used in market to process bastnaesite. In the process, bastnaesite concentrate is heated in a 98% H\(_2\)SO\(_4\) solution to 400 to 500°C for several hours. This decomposes the fluorocarbonate matrix of the bastnaesite, leading to the release of the CO\(_2\) and HF gas. The REE are converted to their sulphates and can be selectively precipitated as Na double sulphates by leaching the residue with NaCl containing water. The sulphate process is currently in use at the Bayan Obo mine in China, while the alkaline method was used by Molycop at the Mountain Pass mine before it closed\(^3\).

Monazite

Monazite is a rare earth phosphate mineral, RE(PO\(_4\)), containing mostly light REE and some heavy REE (more than bastnaesite\(^1\)). Monazite can contain up to 70% REE, primarily Ce and La as well as significant amounts of Nd, Pr and Sm. The Th content is also quite high, ranging from 4 to 12% which is a concern in monazite processing.

As shown in Table 1, the alkaline method is currently one of the main leaching technologies for monazite. The reactions during alkaline leaching are:

\[
\begin{align*}
REPO_4 + 3NaOH & \rightarrow RE(OH)_3 + Na_3PO_4 \\
Th_3(PO_4)_4 + 12NaOH & \rightarrow 3Th(OH)_4 + 4Na_3PO_4
\end{align*}
\]

(4) (5)

After the monazite is digested in 60-70% NaOH at 140-150°C for 4 hours, the residue is dissolved into hot acidic solution, i.e. HNO\(_3\) for solvent extraction using TBP and H\(_2\)SO\(_4\) for solvent extraction using amines of the solution. This process requires proper grinding of the
monazite ore prior to treatment (particle size below 45 μm) so that extraction rates of 98% can be achieved even with relatively low grade ores (Australian monazite 48.6% REE5). However, Th is leached at the same time, which brings radioactive concern of this process. Another concern is the presence of MnIV during alkaline processing, which oxidises Ce and form CeO2, which will not dissolve in HCl4.

An alternative method has been proposed by Merritt5, in which the monazite ore is heated with CaCl2 and CaCO3 under a reducing and sulphidizing atmosphere. This leads to the conversion of REE phosphates to REE oxysulphides (RE2O2S) and oxychlorides (REOCI), while creating a stable Th oxide and chloropatite (Ca5Cl(PO4)3). From this mixture, the REE can be selectively leached with 3% HCl. This process has three advantages over the alkaline process: (1) the conversion step is shorter (45 min vs 3-4 h in the alkaline digestion), (2) there is no necessity for fine grinding, and (3) Th is stabilised as ThO2. However, the REE recovery rate is lower than the alkaline method (89% vs 98%) and the Na3PO4 by-product is not present.

**Ion adsorbed clays**

Ion adsorbed clays are alumina-silicate clays on which REE ions have been adsorbed. Although these clays have an average REE concentration of only 0.05-0.2 wt%, their ease to process and relatively high heavy REE fraction make them a viable REE resource1. These clays require no prior beneficiation process and contain very little radioactive elements, a constant concern with monazite processing.

As given in Table 1, salt or low concentration acidic leaching of these clays to recover REEs is most frequently applied7. (NH4)2SO4 and NaCl are commonly used as the leachants and the leaching reaction is as follows7:

\[
[Al_2Si_2O_5(OH)_4] \cdot RE^{3+} + 3NH_4^+ \rightarrow [Al_2Si_2O_5(OH)_4] \cdot (NH_4^+)_3 + RE^{3+}
\] (6)

The kinetics of the leaching process is very fast, equilibrium is achieved in around 10 min and the total REE extraction is between 80-90%. There have also been leaching trials in Madagascar using seawater as a leachant8. However, these trials yielded recovery rates of around 40%, vastly inferior to the 80-90% achieved with (NH4)2SO4. The industrial process currently used in China uses an ion clay with an REO concentration between 0.08 and 0.8 wt% and a leachant of 7% NaCl and 1-2% (NH4)2SO4 at a pH of 4. A recovery rate of up to 95% REO is achieved9.

**III. Leaching technologies in new and upcoming REE resources**

**REE recovery in the phosphoric acid industry**

The main resource for phosphorous in the phosphoric acid industry is the apatite mineral. This mineral, Ca5(PO4)3(F, Cl, OH), is known to contain 0.1 to 1% REE10. The REE in apatite are present as either REE3+ ions substituted on the Ca2+ ion sites of the apatite lattice (balanced with Na+ ions) or as REE mineral inclusions, e.g. monazite inclusions. As such many of the phosphoric acid producers are seeking to extract the REE as a side stream of their process. The REE are most commonly found in the fluorine variant of the apatite mineral, as such Ca5(PO4)3F will be used as the representative formula in this review.

The main reaction in the phosphoric acid production is as follows11:

\[
Ca_5(PO_4)_3F + 5H_2SO_4 + xH_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot \frac{x}{5}H_2O \downarrow +HF ↑
\] (7)
where $x=0$ for calcium sulphate anhydrate, $x=0.5$ for hemihydrate and $x=2$ for dihydrate (most common). As this completely dissolves the apatite, all REE are transferred into the solution. However, 80% of the REE in solution is lost, due to the precipitation of the insoluble CaSO$_4$ (gypsum). Considering the amount of gypsum formed under typical processing conditions where 5 tonnes of gypsum are formed per tonne of P$_2$O$_5^{12}$, it has promoted several different approaches by phosphoric acid producers to recover the REE.

The first approach was to ignore the REE losses to the gypsum and focus on the REE remaining in solution. This method focuses on the purification of the crude P$_2$O$_5$ (27%) to the commercial grade (54%)$^{13}$. During this process a sludge of CaSO$_4$•\(\frac{1}{2}\)H$_2$O (hemihydrate) forms, which contains the REE. This sludge is leached with HNO$_3$ with a leaching efficiency of around 80%. However, this process is inherently flawed for the production of REE, as most of the REE are lost to the gypsum by-product in the first step. This leads to the second approach, the hemihydrate process$^{12}$, where the process parameters were adapted in order to minimise the REE losses. Since the REE could be leached from the hemihydrate, the process was adapted such that instead of gypsum the hemihydrate is formed during the digestion of the apatite. It was also found that when precipitating the hemihydrate almost all REE are incorporated in the crystals, instead of 80% in the case of gypsum$^{11}$. The hemihydrate is filtered and then leached with diluted H$_2$SO$_4$. This dissolves the hemihydrate and brings the REE into solution. The REE in solution inhibit the re-precipitation of gypsum, allowing for them to be removed through solvent extraction$^{12}$.

Some of the phosphoric acid producers have opted to completely redesign their process in order to make REE recovery easier. Instead of dissolving the apatite using H$_2$SO$_4$, it is dissolved with HNO$_3^{14}$, with Ca(NO$_3$)$_2$ as a by-product. The advantage of this approach is that the solubility of Ca(NO$_3$)$_2$ can easily be controlled, allowing for the REE to be removed from the solution before it is co-precipitated. Also compared to gypsum, Ca(NO$_3$)$_2$ is a marketable product for the fertilizer industry.

Parallel to these developments to extract the REE during the production of phosphoric acid, there have been attempts to process the copious amount of REE containing gypsum already produced by the industry worldwide. In some countries (like Poland$^{15}$) the dumped gypsum represents the largest national REE resource. The most basic process was by leaching the gypsum with 0.5-1M H$_2$SO$_4$ at room temperature$^{10}$. This process leaches about 50% of the REE from the gypsum without destroying the gypsum crystal structure. This process was partially improved by mechanical activation through ball milling the gypsum before leaching$^{16}$. An alternative process uses the following reaction$^{10}$:

$$\text{(NH}_4\text{)}_2\text{CO}_3 + \text{CaSO}_4 \rightarrow \text{(NH}_4\text{)}_2\text{SO}_4 + \text{CaCO}_3$$

All REE are incorporated in CaCO$_3$, which is easily leached with HNO$_3$, also producing useful Ca(NO$_3$)$_2$. Alternatively the CaCO$_3$ can be calcined to CaO and leached with (NH$_4$)Cl leaving an REE rich residue.

**Recycling of lamp phosphor**

Fluorescent lamp phosphors are a valuable REE resource, especially for Y, Eu and Tb. The main REE compounds in these lamps are: Y$_2$O$_3$:Eu$^{3+}$ (YOX), LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$ (LAP),
(Gd,Mg)B₂O₅·Ce³⁺, Tb³⁺ (CBT), (Ce,Tb)MgAl₁₂O₁₉ (CAT) and BaMgAl₁₀O₁₇: Eu³⁺ (BAM). Some also contain chlorapatite (Sr,Ca,Ba,Mg)₅(PO₄)₃Cl:Eu³⁺) and halophosphate (Sr,Ca)₁₀(PO₄)(Cl,F)₂.

Among these REE compounds, the leaching of REE from YOX was found to be the easiest, as they dissolve in relatively diluted acids (0.5M H₂SO₄). In comparison, the REE in the other phosphors can only be leached at a sulphuric acid concentration of 18M. This is due to the fact that the REE in YOX are present as oxides, while the REE in the other phosphors have much stronger chemical bonds. It was found that for these compounds the same leaching processes used in monazite processing were relatively effective. Alternatively a leachant of 4M HCl with H₂O₂ also proved moderately effective.

A typical leaching process of REEs from waste phosphor contains three stages. The ground phosphors are leached with 1.5M H₂SO₄ to dissolve Y and Eu. As it also dissolves some impurities (e.g. Ca, P, Mn, etc.), aqueous ammonia is added to the second stage. This keeps the impurities in the solution while converting the remaining undissolved REE into hydroxides, which precipitate out. The precipitates are leached with HCl in the third stage.

A different approach is the process developed by OSRAM A.G. with a patent in 2011. In this process, the multistep leaching targets specific compounds in the phosphors: 1) leaching with diluted HCl below 30°C leaches only the halophosphates; 2) increasing temperature to 60-90°C, the diluted HCl leaches YOX (alternatively dilute H₂SO₄ can also be used); 3) LAP is then dissolved with concentrated H₂SO₄ above 120°C (but below 230°C); 4) CAT and BAM are dissolved in 30% NaOH at 150°C in autoclave or in molten alkali. For acids, H₂SO₄ is preferred as it dissolves fewer impurities (Ca and Sr) compared to HCl or HNO₃. Also ultra sound increases the efficiency, regardless of the leachant.

**Recycling of magnet scrap**

There are two major REE to be recovered from REE magnets: Nd from NdFeB magnets and Sm from SmCo magnets. Most recycling efforts of magnets are currently focused on the production waste (so called swarf). As such the input streams for magnet leaching are relatively pure. The leaching of SmCo swarf is relatively easy. It can completely dissolve in 3M HCl, HNO₃ or H₂SO₄. Processes for SmCo leaching have not been further developed as the magnets have fallen out of favour with the rise of the NdFeB magnets.

For the NdFeB magnets two different leaching routes are established: a total leaching route and a selective leaching route. In the total leaching route the whole swarf is dissolved with the aim to separate the Nd afterwards. Similar to the SmCo swarf, this is relatively straightforward as NdFeB easily dissolves in the three mineral acids. The choice of acid is mostly dependent on the subsequent separation process: H₂SO₄ for selective precipitation and HCl for solvent extraction. HNO₃ is avoided since it produces nitrated waste water. Note that the solubility of rare earth elements decreases with increasing temperature, leading to lower leaching efficiencies with increasing temperature. As the leaching efficiency is more important than leaching rate in magnet recycling, room temperature is preferred.
In the selective leaching process, Nd is extracted from the magnets without dissolving Fe and B. This is achieved through roasting and leaching. The roasting is based on the Pourbaix diagram (fig. 1). A joint stability region of Nd$^{3+}$ and Fe$_2$O$_3$ within the pH range from around 1 to 7 in the diagram can be observed. Using a roasting condition of 6 h at 900°C in air and followed by a 0.02M HCl leaching, an extraction rate of 99% of Nd and less than 0.5% of Fe was achieved$^{19}$, while the same process without the roasting leached over 50% of the Fe.

IV. Recent progress and new leaching technologies for REE leaching

Progress in bastnaesite leaching

The environmental pollution caused by fluorine emissions during H$_2$SO$_4$ roasting of bastnaesite processing in China is becoming an increasing concern$^{23}$. Due to this, processes have been developed to prevent the emission of fluorine. A first method revolves around only leaching the carbonate REE while leaving the REE fluorides in the residue. This is achieved by thermally activating the ore (400°C for 3 h) and then leaching it with HCl. The thermal activation enables the leaching of the carbonates at conditions in which the fluorides are unaffected. The reported leaching efficiency of this process is 94.6% for the carbonates and 0.07% for the fluorides$^{23}$.

A different method involves progress in the air roasting process mentioned in section II. This process had already been proven ineffective in leaching the fluoride components, but the oxidation of Ce$^{III}$ to Ce$^{IV}$ prevented Ce from being leached together with the other REE and led to purification issues. The addition of thiourea$^{24}$ offered a solution to this problem. Thiourea prevents the oxidation of Ce, keeping it trivalent after roasting and thus allowing it to be leached with HCl together with other REE. This allowed for the recovery of Ce and the non-fluoride bonded REE. These methods are inherently wasteful however, since not all REE present in the bastnaesite are leached.

Another more efficient process involves the mechanochemical activation of bastnaesite by milling it with NaOH powder$^{25}$. In this process the bastnaesite concentrate is milled together with NaOH powder, followed by washing with water to remove the Na compounds and then leaching with HCl. These steps are performed at room temperature and can lead to a leaching efficiency of around 90%.

![Pourbaix diagram Fe-H$_2$O and Nd-H$_2$O system$^{19}$](image-url)
Bioleaching

The field of bioleaching is being explored for REE extraction from low grade sources. The REE concentration of the sources is often below the 1% level, mostly around 0.5%. These sources include old mine tailings and ion adsorbed clays. As total leaching of these sources, using strong mineral acids and/or bases, leads to large amounts of waste and is very inefficient, alternative low cost routes are being explored. In Egypt the possibility of using 'Acidithiobacillus ferroxidans' (a bacteria often used in the bioleaching of copper26) to bioleach low grade Gibbsite ore to recover the REE (0.49%) and U (0.05%) has been investigated27. Their initial results show a leaching efficiency of about 55% for REE and 49% for U. Other bacteria that are tested are 'Aspergillus ficum' and 'Pseudomonas aeruginosa'28 leading to slightly higher leaching efficiencies for REE’s, around 75%.

Researchers in Japan have investigated the use of a blue-green algae named 'phormidium' in combination with (NH4)2SO4 for the extraction of REE from ion adsorbed clays29. In this process the ammonium ions displace the adsorbed REE3+ ions in the clays bringing them into solution, as well as several other adsorbed ions, mainly Al, Mn and Si. This solution is then brought into contact with dried and ground algae, which selectively adsorb the REE ions. Leaching efficiencies between 40% (Dy, Gd) and 70% (Nd, Sm), dependent on the REE species, could be obtained. The advantage of this process is that temperature and pH control is easy and the leaching time is relatively short compared to other bioleaches (3 h vs several days). Also, in Japan 'phormidium' is easily obtained as it needs to be removed from the local reefs to preserve them. The waste of this process is also minimal and easily detoxified.

Microwave assisted leaching

Microwave assisted leaching is frequently used for improving mineral leaching efficiency30. For REE extraction however no concrete results have been found yet. The principle of microwave assisted leaching is based on the fact that metal-containing minerals are less transparent for microwaves than gangue minerals such as CaO, CaCO3 and SiO230. This leads to on-site heating at and around the metal-containing mineral, thus locally changing the leaching kinetics. As the leaching kinetics generally increase with increasing temperature this would lead to increased leaching rates at the metal-containing minerals, allowing the leaching to be finished sooner and with less unwanted dissolved species originating from the gangue. Another effect of the localised and rapid heating is that it can fracture the metal-containing mineral surfaces due to thermal stresses, thereby effectively increasing the surface area31. While microwave leaching has not yet been applied to REE leaching, it has been applied to Cu leaching from chalcopyrite and to Au leaching31. The effects observed there, e.g. removing reaction product from the surface through convective streams (Cu) or activating finely distribute metal-containing areas (Au), can be beneficial for REE leaching. Considering these current applications there is potential in applying microwave heating to REE leaching, especially for low grade sources where the REE are finely distributed in the material, sometimes in hard to leach compounds (e.g. phosphates), such as in old mine tailings.
V. Conclusions
This brief review shows that there is a variety of leaching technologies that have been developed in the past years, both for primary REE minerals and secondary resources. These in-market technologies were developed according to the mineralogy, REEs occurrence and engineering feasibility. The main features are that these are all multi-step processes and that both acid and alkaline are often interactively used in a single process. In view of the increasing importance of secondary REE resources, this overview of current state-of-the-art technologies can provide a basis for developing more efficient processes for REE recovery from secondary resources, i.e. mine tailings and magnet scraps. For example, old mine tailings often contain a sizeable fraction of apatite and/or monazite. Drawing inspiration from current monazite processing and phosphoric acid production can lead to a workable process for REE recycling from these tailings. As for WEEE, many individual elements (e.g. lamp phosphors and magnet swarf) of WEEE have been looked at for REE recycling, but not a general WEEE stream. However, knowledge of these individual components will be invaluable to develop a process for a mixed WEEE stream. The main challenges will be overcoming the dilution effect of REE, both in the tailings and in the mixed WEEE, and the variety of contaminants. Here advancements in microwave leaching or bioleaching show promise.

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References
Extraction of lanthanides from spent polishing agent

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Abstract

The polishing of glass substrates or wafers requires the usage of fine grained particles based on lanthanides. During processing the sludge becomes enriched with different elements depending on the specific production program. However, concentrations of impurities can reach critical values and may influence the surface quality of the substrates in a negative way. Therefore, the polishing agents have to be removed from the system and recycled meaningfully. The paper describes ways of processing such secondary RE resources using different hydrometallurgical methods including mineral acids for the extraction. Finally, the focus was set on the evaluation of precipitation methods for the production of a rare earth concentrate.

Introduction

Polishing agents and additives used in the glass industry are estimated to represent a global demand of rare earths (RE) of approximately 10 % in terms of economic value but mainly consist of light rare earths cerium and lanthanum¹,²,³. These most abundant RE have suffered from continuously falling prices (Figure 1) in the last years which makes economic recycling difficult.

Figure 1: Relative price development of various REO from 2012 to 2014⁴
Based on the price level in January 2012 which was set to one, the changes in price are visualized as dimensionless values ($\varepsilon_{xx/2014}/\varepsilon_{01/2012}$). As can be seen from the chart the costs for many of the REOs are less than 40% of the price at the beginning of 2012. Therefore, it seems to be of high relevance to design easy manageable, environmentally friendly and low-cost recycling processes. In contrast the strategic independence of the European Union and many other countries outside Europe from China’s RE supply is a strong driving force for numerous recycling projects. Kato 5 suggested an alkaline treatment of spent polishing material using 4 mol/kg sodium hydroxide solution and temperatures between 50 to 60 °C. Thus, impurities such as silicon dioxide and alumina dissolve and can be separated from the solution by heating and precipitation as zeolites 5. Matsui 6 also treated abrasives with solutions of sodium hydroxide to achieve dissolution of for example $\text{SiO}_2$. Further processing includes a precipitation respectively a promoted settling of fine disperse cerium oxide particles with for example aluminium sulphate. Subsequent to the removal of the supernatant the precipitates are washed several times. Additionally, the pH of the resulting fraction is adjusted to low acidic or neutral in order to remove soluble impurities 6. An advanced process is proposed by Moon 7 also dealing with the removal of contaminants from a spent polishing agent by a caustic soda solution. Small amounts of sodium fluoride and sodium carbonate support the purification process 7.

A dry process was introduced by Ozaki 8 using carbo-chlorination techniques to achieve extraction of the rare earths from a material basically consisting of 38 wt.-% $\text{CeO}_2$, 28 wt.-% $\text{La}_2\text{O}_3$ and 10 wt.-% $\text{Nd}_2\text{O}_3$ together with alkaline earth metal oxides, silicon dioxide and fluorine. Subsequent chemical vapour deposition experiments using $\text{Al}_2\text{Cl}_6$ as complexing agent showed that specific temperature gradients may lead to a separation of rare earth chlorides from formed aluminium and iron chlorides. Enrichment of single rare earth chlorides can be obtained by a repeated CVT process 8.

Nevertheless, processes using solutions of sodium hydroxide face problems concerning the quantitative dissolution of silicon dioxide and metallic components which originate from semiconductor polishing. The application of chlorine in the process may result in the separation of the rare earths, but careful material selection of the reactor lining has to be done due to the highly corrosive media. Therefore, acidic hydrometallurgical methods seem to be favourable. One available technology is used at Hydrometal in Belgium 9. The rare earth compounds of spent polishing agents are dissolved by nitric acid in combination with hydrogen peroxide acting as a reducing agent for $\text{Ce(IV)}$ in this case. The addition of oxalic acid leads to the precipitation of the RE oxalates 9. As it is shown later, our own experiments confirm the possibility of good cerium extraction by these chemicals, but also illustrated limited lanthanum dissolution.
Experimental

Input material
The material of interest was a typical polishing material based on lanthanides with an approximate composition according to Table 1. The major impurities which make a recycling necessary are the oxides of silicon, zinc, sodium and calcium because they may cause decreasing surface qualities of the glass substrate at critical values.

Table 1: Chemical composition of the used abrasive material

<table>
<thead>
<tr>
<th>Oxide</th>
<th>wt.-%</th>
<th>Oxide</th>
<th>wt.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>69</td>
<td>SiO₂</td>
<td>11</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>8</td>
<td>ZnO</td>
<td>2</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>1</td>
<td>P₂O₅</td>
<td>2</td>
</tr>
<tr>
<td>CaO</td>
<td>1</td>
<td>Na₂O</td>
<td>1</td>
</tr>
</tbody>
</table>

Experimental set-up
All leaching and extraction experiments were carried out at atmospheric pressure in three-neck round-bottom flasks using a heating mantle and temperature control. Furthermore, condensers and dropping funnels were employed. The experimental set-up for the leaching tests can be seen in Figure 2. Nitric and hydrochloric acid tests were carried out under continuous agitation. Sulphuric acid experiments show onward solidification of the sludge consisting of the polishing agent and the concentrated acid at raising temperatures.

Figure 2: Experimental set-up for the extraction experiments (Figure drawn with ACD/ChemSketch)
Precipitation experiments were performed from hydrochloric and sulphuric acid solutions. These were carried out in beakers at room temperature under continuous stirring. Frits of porosity 4 (10-16 μm mesh) separated the leaching residues and precipitation products from the liquid phase. Both solid fractions were dried at 120 °C and calcined if it was assumed that the obtained compounds differ from oxides.

Nitric acid leaching

The experiments included a number of leaching experiments to determine the most important parameters. As nitric acid - an oxidizing acid - was used, hydrogen peroxide had to be added in order to reduce tetravalent cerium from CeO₂ to the cerous state. The experiments started with the addition of nitric acid to 50 g of spent polishing material. After a heating period 100 g H₂O₂ (30 wt.-%) were added. Different amounts and concentrations of nitric acid were tested and the temperature and leaching time were varied (Table 2). Subsequently, filtration and washing of the filter cakes were done. Additionally, the solid residue was dried, the dissolved mass measured and the material was analysed by XRF.

Table 2: Basic parameters for HNO₃ experiments

<table>
<thead>
<tr>
<th>Acid</th>
<th>Concentrations tested [wt.-%]</th>
<th>Additional chemicals</th>
<th>Temperatures tested during leaching [°C]</th>
<th>Leaching time [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>47, 65</td>
<td>H₂O₂</td>
<td>70, 90</td>
<td>1, 6, 12</td>
</tr>
</tbody>
</table>

Hydrochloric acid leaching

Hydrochloric acid leaching tests started in the same way as the nitric acid leaching experiments. As HCl is a reducing acid, the strength of the chlorine ion was assumed to be strong enough for complete reduction of Ce⁴⁺. Therefore, the amount of hydrogen peroxide was varied as well. An overview of tested parameters in the leaching step is given in Table 3.

Table 3: Basic parameters for HCl leaching experiments

<table>
<thead>
<tr>
<th>Acid</th>
<th>Concentrations tested [wt.-%]</th>
<th>Additional chemicals</th>
<th>Temperatures tested during leaching [°C]</th>
<th>Leaching time [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>16, 21, 32</td>
<td>H₂O₂</td>
<td>80, 95</td>
<td>4, 8</td>
</tr>
</tbody>
</table>

The pregnant leach solutions were adjusted to a volume of 500 ml. Subsequently, precipitation experiments using the total amount of the leaching liquor and oxalic acid were done. This step was supported by Design of Experiments which makes a statistical analysis possible. While the leaching parameters were held on a constant level (Table 4) the amounts and concentrations of oxalic acid solutions were modified. After the conversion of the precipitation product to a mixed rare earth oxide by thermal treatment at 750 °C and the XRF analysis of the product, mass balances were calculated. The yields for each element represent...
the raw data for the statistical analysis. As a consequence of the constant leaching parameters, the result of the statistical analysis gives accurate data about the precipitation step.

Table 4: Leaching parameters for subsequent precipitation

<table>
<thead>
<tr>
<th>Pol. Agent [g]</th>
<th>c(acid) [wt.-%]</th>
<th>H2O2 [g]</th>
<th>Temperature [°C]</th>
<th>Leaching time [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>32</td>
<td>100</td>
<td>80</td>
<td>4</td>
</tr>
</tbody>
</table>

A flowsheet of the entire HCl leaching and precipitation process can be found in Figure 3.

![Figure 3: Process flowsheet of hydrochloric acid leaching and oxalic acid precipitation](image)

Test execution for experiments using sulphuric acid

The experimental procedure and set-up correspond to the above described in many ways. One major difference between nitric or hydrochloric leaching experiments from the sulphuric acid process is the extraction of lanthanides in two steps including a digestion and subsequent elution of formed RE sulphates. The digestion was performed in round-bottom flasks as it was described earlier. During this process at temperatures between 100-200 °C the slurry consisting of polishing agent and concentrated sulphuric acid suffers from onward solidification. Therefore, contrary to HNO3 and HCl experiments stirring during the entire digestion period became impossible. The digested materials were subsequently leached at room temperature with sufficient amount of water and transferred to frits. The filter cakes were washed several times, dried, calcined and finally analysed.
The pregnant red-orange leaching solutions were subsequently transferred to beakers and treated with different precipitation agents to achieve mixed RE-compounds. The universally valid process flowsheet can be seen in Figure 4.

![Diagram](image)

**Figure 4:** Sulphuric acid digestion and production of a mixed REO concentrate

**Results**

**Nitric acid leaching experiments**

Nitric acid leaching experiments showed the possibility of cerium dissolution up to 90%. Nevertheless, it could be found that lanthanum extraction is insufficient and limited to 60-70%. The investigations also revealed the results from Figure 5a and 5b. Decreasing solid/liquid ratios induced increasing reduction of the initial mass of the input material which correlates to the extraction of cerium and lanthanum and therefore higher extraction rates can be achieved. Figure 5b shows the effect of extended leaching periods.
Another comparison between the experiments visualises the effect of a change in leaching temperature. An increase in temperature from 70 to 90 °C does not lead to intensified dissolution. Moreover, an increase in acid concentration shows no effect on the extraction (Figure 6).

**Figure 6: Influence of temperature and acid concentration on the dissolution of the input material**

**Hydrochloric acid leaching and precipitation experiments**

Some obtained results from nitric acid leaching experiments coincide with data from HCl leaching. On the one hand, good extraction of cerium is possible under optimum leaching conditions. On the other hand the extraction of lanthanum is limited to 60-75 % as well. XRD analysis of the leaching residues revealed that mainly fluoride and phosphate compounds of lanthanum remain undissolved. Further investigations of the leaching step showed decreasing influence of H₂O₂ at larger excess and concentration of HCl. 50 % excess of acid equals a mass of 43.75 grams of HCl whereas the amount of added solutions varied depending on their concentration. As a result 50 % excess required 136.73 grams of 32 wt-% HCl.
Figure 7: Ce extraction as a function of acid concentration and amount of H₂O₂

Precipitation experiments required leaching operations at constant parameters. Therefore, these tests were performed using solutions won by leaching of 50 g of polishing agent with 273.45 g HCl (32 wt.-%) which represents an excess of 200 % and 100 g H₂O₂ (30 wt.-%). After filtration the solutions were adjusted to volumes of 500 ml and transferred to oxalic acid processing. 30 to 50 g of oxalic acid were used in this process in concentrations of 50, 62.5 and 80 g/l H₂C₂O₄ corresponding to approximate excesses of the chemical of 0 to 66 %. The calculation took into account that on average 97 % of cerium, 70 % of lanthanum and 54 % of zinc present in the raw material can be extracted under the applied leaching conditions and form oxalates. Later the XRF analysis of the precipitation products showed that zinc remains in the solution. Subsequent to the above described thermal treatment and XRF analysis of the obtained mixed RE-oxide the elemental yields were determined. The result of the statistical analysis is shown in Figure 8.
As can be seen from the plots above the excess of oxalic acid added to the leach liquor strongly affects the yields of Ce and La whereas there are some statistical uncertainties concerning the influence of the concentration. Nevertheless, increasing acid concentrations tend to support the formation of Ce oxalates, whereas the isolation of lanthanum decreases. The low yields for lanthanum are caused by the above mentioned limitation of the extraction. A representative chemical composition of a final product won by the described leaching and precipitation process can be found in Table 5.

Table 5: Representative XRF analysis of an oxide product

<table>
<thead>
<tr>
<th>Oxide</th>
<th>wt.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>90.73</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>8.57</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.08</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.074</td>
</tr>
<tr>
<td>CaO</td>
<td>0.07</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Sulphuric acid leaching and precipitation experiments

The experiments revealed that sufficient sulphuric acid and temperature must be applied to the process for quantitative digestion of the spent abrasive. Furthermore, complete elution of formed sulphates requires enough water and repeated washing of the filter cakes. Optimum digestion and leaching conditions led to extraction rates of almost 99 % for Ce and 98 % for La. Figure 9 shows the filtration and washing of a digested polishing agent. However, the solutions won by this process show the disadvantage of low stability and precipitation of lanthanide salts within a couple of hours. Therefore, the further treatment with precipitation agents had to be done quickly. The products won by the application of commercial precipitation agents met the specifications for additional processing.
Conclusions

Three ways of processing polishing materials were tested. The focus was mainly set on the extraction of lanthanides from the raw material, whereas all mineral acids of technical relevance were taken into account. Nitric and hydrochloric acid experiments showed strongly limited dissolution of lanthanum compounds. The extraction of cerium as most of it was present in its tetravalent stage necessarily requires a reducing agent in the case of HNO₃ leaching. Hydrogen peroxide was chosen as reducing agent because the resulting leach liquor is thereby not contaminated by foreign ions. Under certain conditions almost complete cerium extraction could be achieved by hydrochloric acid leaching without the use of H₂O₂. Especially high HCl concentrations affect the dissolution of cerium in a positive way. Oxalic acid as a well-known precipitation agent for rare earth elements was chosen because of its advantage to form precipitation products at low pH values. Therefore, the contamination of the obtained products from hydrochloric solutions could be reduced. Additional experiments using concentrated sulphuric acid pointed out higher lanthanum extraction than was achieved for the previously described tests. However, digestion of the polishing material and subsequent leaching of formed water-soluble cerium and rare earth sulphates require significantly higher temperatures (up to 200 °C) and larger amounts of washing water respectively.

Acknowledgements

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THE REE POTENTIAL IN “URBAN” ORE DEPOSITS: AN EVALUATION ON CONTENTS AND PROSPECTING TOOLS FROM ITALIAN MUNICIPAL SOLID WASTE INCINERATORS.

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Abstract

Solid residues from Municipal Solid Waste Incinerators (MSWI) may represent an unconventional source of REE and other critical raw materials as defined by the European Commission. In this contribution we present the total REE content in bottom and fly ashes, which are the common MSWI outputs, and their estimated annual flow are significant. Samples were digested with sodium peroxide sintering which is highly effective analytical technique and the analysis was performed with ICP-MS. Bottom and fly ashes have an average concentration of 103 and 54 mg/kg $\Sigma$REY, respectively. For fly ashes the expected annual flow is 1.1 t/a LREE and 0.3 t/a HREE, whereas for bottom ashes is 22.5 t/a LREE and 5.2 t/a HREE. Moreover, we show that simple magnetic susceptibility measurements can be a promising prospecting method when exploring for REE in urban ores is concerned.

Introduction

The European Commission defined a list of “critical” raw materials on the basis of their relative economic importance and supply risk [1]. Rare Earth Elements (REE) are among critical raw materials because of their importance for the new and green technologies, e.g. in magnets for wind turbines, hybrid car engines, etc [2]. Traditionally, the main sources of REE are natural ore deposits, usually divided into primary (e.g., igneous rocks, hydrothermal related deposits), secondary deposits (e.g., placers, lateritic soils) and by-product productions from other mining operation. The major REE ore deposits are located in a few countries namely China and Mongolia [1, 2]: restriction policies on the REE export from these countries may increase the supply risk for EU countries as occurred during the 2011 crisis. For these reasons there is an increasing effort to evaluate other REE sources. In a recent work it has been demonstrated that solid residues from incinerated municipal waste host interesting amounts of critical raw materials [3]. Here we present the total elemental chemistry of bottom and fly ashes from two Italian incineration plants and the calculated REE annual flow [4] and magnetic data results.
Materials and Methods

Sampling
Final solid residues from two waste incinerator plants from Northern Italy, named plant A and B were collected. The selected incinerators have similar incineration systems consisting of two lines that drive the collected waste, about 120000 t/a, in the furnace that operates at temperatures between 850 and 1100 °C. More than 90% of the solid waste input is made of unsorted municipal solid waste.

The main outputs of the incineration process are slags, bottom and fly ashes. Belt conveyors transport the slags and bottom ashes (hereafter BA) to a temporary outdoor storage site where the BA are piled up. Directly from the BA storage site, 7-8 kg primary sample was taken; the batch was split in four portions, the opposite portions were mixed together and again split for three times, to ensure homogeneity. Fly ash and APC residues (hereafter, FA) have been separately sampled at the different devices from the two incinerators. Where it was possible, FA were collected at the furnace, after the mechanical waggle and after the bag filter (with soda or lime additives). In both incinerator plants, about 5 kg FA primary sample was collected with a random sampling method from big bags and blended from a large number of increments in order to reach representativeness. The overall process ensures that there is no mixing between FA and BA.

Analytical techniques
The complete sample digestion was obtained with the sodium peroxide sintering mainly of protocol as in [5] and major and trace elemental analysis was made with ICP-MS (7500ce Agilent Technologies). Analyses were performed at the department of General and Analytical Chemistry of Montanuniversität Leoben (Austria).

Magnetic susceptibility measurement were carried out by using a dual frequency MS2B Bartington meter available at the Institute of Marine Sciences (CNR, Bologna). Dried and milled (<40 μm) samples of MSWI residues were laid down and gently compacted in the sample holder. The exact sample mass was recorded and magnetic susceptibility values on MS2B display were noted. Mass specific magnetic susceptibility (χ) was calculated dividing κ, i.e. the ratio between the induced magnetisation and external magnetic field, by the sample mass. κ, previously corrected for the drift, is expressed in $10^{-5}$ SI units, whereas χ in m$^3$kg$^{-1}$.

Substance flow analysis
An estimation of substance flow [4] for plant A and B residues was carried out to determine the REE annual flow within output products. The spatial system boundary for the experiment was the MSWI process itself, from the waste collection to outputs products, and included the sampling. The temporal system boundary was defined as 1 year, assuming that the sampled material is representative for one year process activity. For the calculation of total annual flow, F in kg/a, for BA and FA we used the following equation:
\[ F = C_i \cdot O \quad (Eq. \ 1) \]

where: \( C_i \) is the measured concentration of element \( i \) in mg/kg and \( O \) is the total output mg/a for the BA and FA.

**Results and discussion**

**Statistical data screening**

The variation of REE in each sample, both for BA and FA, has been analysed using the box plots (Fig. 1). The general variability may reflect the heterogeneity of the samples, resulting from different waste input, treatment steps and combustion condition between the two incineration facilities. In BA samples the majority of REE have concentration from around 0 mg/kg (25th percentile) to 15 mg/kg (75th percentile) while in FA from 0 (25th percentile) to 5 mg/kg (75th percentile) (Fig. 2a). Fig. 2b shows that light REE (LREE: Sc, La, Ce, Pr, Nd, Sm, Eu, Gd) and heavy REE (HREE: Y, Tb, Dy, Ho, Er, Tm, Yb, Lu) are higher in BA residues than in FA, probably due to the wide range of process treatments (e.g. different cooling conditions, chemical additives).

**Figure 1:** The REY variability in the studied samples. The boundaries of the box indicate the 25th percentile and the 75th percentile, the continuous line within the box marks the median and the red dot marks the mean. Whiskers above and below the box indicate the 90th and 10th percentiles, whereas starred dots are the outliers (mainly Ce).

**Figure 2:**

a) Boxplot of REE

b) Boxplot of REE, HREE, LREE
**Figure 2:** a) Comparison of REE contents in BA and FA samples between incinerators A and B; outliers, mainly Ce and La, are shown with starred dots. b) ∑REE, ∑HREE and ∑LREE in BA and FA samples. For the significance of box-plots see Fig. 1.

In order to understand the difference of REE concentration between plants A and B independent sample t-test was conducted (Tab. 1).

Considering the total of MSWI residues and FA residues the mean contents of REE for the two incinerators are statistically equal. On the other hand the REE means in the BA residues is significantly (at 0.05 significance level) different between plant A and B, in spite of the similar incineration process. This is probably due to a more impacting nugget effect.

**Table 1:** Comparison of the REE mean content in MSWI residues from plants A and B. Tests for FA and bulk MSWI (BA+FA) residues have been calculated but not reported.

<table>
<thead>
<tr>
<th>REE</th>
<th>Equal variance</th>
<th>k-squared</th>
<th>p-value</th>
<th>t</th>
<th>p-value (two-tailed)</th>
<th>Mean A</th>
<th>Mean B</th>
<th>95% confidence interval</th>
<th>Lower</th>
<th>Upper</th>
</tr>
</thead>
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<tr>
<td>Ce</td>
<td>Not assumed</td>
<td>1.75</td>
<td>0.19</td>
<td>2.80</td>
<td>0.01</td>
<td>32.93</td>
<td>30.53</td>
<td>0.60</td>
<td>4.19</td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>Assumed</td>
<td>8.34</td>
<td>0.00</td>
<td>7.11</td>
<td>0.00</td>
<td>2.06</td>
<td>1.63</td>
<td>0.30</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>Not assumed</td>
<td>0.84</td>
<td>0.36</td>
<td>6.12</td>
<td>0.00</td>
<td>1.33</td>
<td>1.07</td>
<td>0.17</td>
<td>0.35</td>
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</tr>
<tr>
<td>Eu</td>
<td>Assumed</td>
<td>3.98</td>
<td>0.05</td>
<td>5.31</td>
<td>0.00</td>
<td>0.97</td>
<td>0.84</td>
<td>0.08</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
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<td>8.22</td>
<td>0.00</td>
<td>4.43</td>
<td>0.00</td>
<td>2.18</td>
<td>1.93</td>
<td>0.13</td>
<td>0.37</td>
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<tr>
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<td>Assumed</td>
<td>5.24</td>
<td>0.02</td>
<td>8.76</td>
<td>0.00</td>
<td>0.42</td>
<td>0.32</td>
<td>0.08</td>
<td>0.13</td>
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</tr>
<tr>
<td>La</td>
<td>Not assumed</td>
<td>0.91</td>
<td>0.34</td>
<td>4.68</td>
<td>0.00</td>
<td>19.30</td>
<td>16.13</td>
<td>1.75</td>
<td>4.58</td>
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</tr>
<tr>
<td>Lu</td>
<td>Assumed</td>
<td>16.00</td>
<td>0.00</td>
<td>5.25</td>
<td>0.00</td>
<td>0.18</td>
<td>0.13</td>
<td>0.03</td>
<td>0.06</td>
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<td>0.09</td>
<td>-0.93</td>
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<td>13.07</td>
<td>13.68</td>
<td>-1.97</td>
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<td>0.01</td>
<td>2.39</td>
<td>0.03</td>
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<td>3.20</td>
<td>0.05</td>
<td>0.68</td>
<td></td>
</tr>
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<td>Sc</td>
<td>Assumed</td>
<td>7.55</td>
<td>0.01</td>
<td>3.50</td>
<td>0.00</td>
<td>12.92</td>
<td>9.93</td>
<td>1.20</td>
<td>4.78</td>
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<td>Sm</td>
<td>Assumed</td>
<td>4.38</td>
<td>0.04</td>
<td>4.91</td>
<td>0.00</td>
<td>2.35</td>
<td>2.05</td>
<td>0.17</td>
<td>0.42</td>
<td></td>
</tr>
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<td>0.41</td>
<td>2.94</td>
<td>0.01</td>
<td>0.43</td>
<td>0.39</td>
<td>0.01</td>
<td>0.07</td>
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<td>0.00</td>
<td>6.38</td>
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<td>0.13</td>
<td>0.03</td>
<td>0.05</td>
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<td>Y</td>
<td>Not assumed</td>
<td>2.35</td>
<td>0.13</td>
<td>5.44</td>
<td>0.00</td>
<td>14.97</td>
<td>12.53</td>
<td>1.50</td>
<td>3.38</td>
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<td>Yb</td>
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<td>10.90</td>
<td>0.00</td>
<td>6.69</td>
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<td>1.21</td>
<td>0.90</td>
<td>0.21</td>
<td>0.41</td>
<td></td>
</tr>
</tbody>
</table>

*Numbers smaller than 0.05, significance level, are in bold character*

**Correlations with major and trace elements**

Correlations between ∑REE and selected major and trace elements (Fig. 3), demonstrate that volatile and soluble components (e.g. Cd and K₂O, respectively) do not control the REE contents, but allow to distinguish BA from FA. The most of volatile elements, e.g., Bi, As, Cd, Sb, Sn has a similar behaviour. Conversely, major elements like P₂O₅ (of likely anthropogenic introduction) and Al₂O₃ (both geogenic and anthropogenic component) show a positive correlation with ∑REY.
Correlation with magnetic properties

Heavy metals are known to have affinity to form metallic bonding with ferrous material, which leads to increase the magnetic susceptibility. Correlations between magnetic data and heavy metals concentration are often observed, e.g. [6, 7]. In case of MSWI residues, mass specific magnetic susceptibility is also related to iron oxide mass fraction. Furthermore we found positive correlation with REE, both LREE and HREE (Fig. 4). This correlation could be linked to the presence of REE-bearing devices in waste input (e.g., NdFeB magnets). A better comprehension of the relation between the REE and susceptibility requires further study; at this stage the aim is to understand whether the magnetic properties can be a quick and inexpensive indicator of the REE presence in MSWI residues.

Each scatter plot allows to distinguish BA from FA samples, which are higher and lower than 1000-10-8 m3/kg, respectively. FA from bag filters (FAS and FAL) have the lowest REE content, which usually correspond to lowest χ values. High magnetic values do not necessarily reflect an high REE content; rather around the 2000 χ value there is the highest density of samples with high amounts of REE.
Figure 4: ΣLREE and ΣHREE vs. mass specific magnetic susceptibility ($\chi$). Data set is grouped by kind (BA=bottom ash; FAE=fly ash from ESP; FAL=fly ash from bag filter with Ca-additive; FAS=fly ash from bag filter with Na-additive; FAU=untreated fly ash) and provenance (A=plant A; B= plant B).

**Mass flow analysis**

With the simple mass balance given by the equation 1, we estimated the yearly flows of REE, in kg/a, for the incinerators A and B (Tab. 2). The measured concentrations are provided by ICP-MS analyses. The owners of the incinerator plant provided the total BA and FA output. We assumed that the sampled material is representative for one-year process activity (i.e., 2013).

Figure 5: Pie charts of LREE and HREE; the partitioning of mean concentrations and mean flows between the different outputs are reported.

The REE mean concentrations are quasi-equally distributed between the different kind of MSWI residues. However, the estimated yearly mean flows is extremely high in BA (Fig. 5). An
individual estimation of BA flows is indispensable for each incinerator because of the high heterogeneity of sample materials and sampling bias and as a consequence of t-test results. In the following table we decided to report BA flows for plants A and B with their standard deviation values (on the basis of the samples batch). Flows from each kind of FA and the mean flow of FA residues from the two plants are reported.

<table>
<thead>
<tr>
<th>REE</th>
<th>FAS (A)</th>
<th>FAU (A)</th>
<th>FAL (A)</th>
<th>FAU (B)</th>
<th>FAL (A)</th>
<th>FAU (B)</th>
<th>FAE (B)</th>
<th>BulkFA (A,B)</th>
<th>BA (A)</th>
<th>BA (B)</th>
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<tr>
<td>Ce</td>
<td>50</td>
<td>455</td>
<td>359</td>
<td>669</td>
<td>827</td>
<td>600</td>
<td>464</td>
<td>7590 ±600</td>
<td>10149</td>
<td>±497</td>
</tr>
<tr>
<td>Dy</td>
<td>2</td>
<td>19</td>
<td>28</td>
<td>35</td>
<td>43</td>
<td>26</td>
<td>23</td>
<td>453 ±48.5</td>
<td>546</td>
<td>±8.50</td>
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<tr>
<td>Er</td>
<td>1</td>
<td>14</td>
<td>15</td>
<td>19</td>
<td>24</td>
<td>15</td>
<td>14</td>
<td>303 ±29.9</td>
<td>373</td>
<td>±12.7</td>
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<tr>
<td>Eu</td>
<td>1</td>
<td>17</td>
<td>13</td>
<td>22</td>
<td>26</td>
<td>19</td>
<td>15</td>
<td>219 ±19.2</td>
<td>275</td>
<td>±17.1</td>
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<td>29</td>
<td>67</td>
<td>42</td>
<td>124</td>
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<td>42</td>
<td>501 ±47.0</td>
<td>647</td>
<td>±33.3</td>
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<td>7</td>
<td>5</td>
<td>6</td>
<td>8</td>
<td>5</td>
<td>5</td>
<td>94 ±10.2</td>
<td>107</td>
<td>±0.20</td>
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<td>33</td>
<td>41</td>
<td>41</td>
<td>57</td>
<td>57</td>
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<td>5290</td>
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<td>4576</td>
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<td>2960</td>
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<td>6</td>
<td>100 ±10.8</td>
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<td>2</td>
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<td>2</td>
<td>1</td>
<td>10 ±4.8</td>
<td>14</td>
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<td>4207</td>
<td>±200</td>
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<td>15</td>
<td>13</td>
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<td>300</td>
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<td>994.0</td>
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<td>19300 ±2050</td>
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<td>±1700</td>
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<td>±200</td>
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<td>1068.0</td>
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<td>20600 ±2200</td>
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<td>1787</td>
<td>1452</td>
<td>24000 ±2400</td>
<td>31400</td>
<td>±1900</td>
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[FAS=Fly ash from bag filter with Na-additive; FAU=Fly ash untreated; FAL= Fly ash from bag filter with Ca-additive; FAE= Fly ash from electrostatic precipitator (ESP); bulkFA=mean flow of fly ashes; BA=Bottom ash; A and B are the selected WTE plants]

Considering to fig. 5 and table 2, the FA residues from bag filters (with chemical additives) have very low potential of REE flow. Bottom and fly ashes have an average concentration of 103 and 54 mg/kg ΣREE, respectively. For fly ashes the expected annual flow is 1.1 t/a LREE and 0.3 t/a HREE, whereas for bottom ashes is 22.5 t/a LREE and 5.2 t/a HREE. The data of annual flows are in good agreement with recent works [3].

As a semi-quantitative index to evaluate the economic feasibility, we compare the typical cutoff values used in the mining industry. The minimum cut-off grade for naturally occurring REE oxides is 0.2 wt.% [9], while this study shows a REE grade of 0.01 wt%. Numbers seem unfavourable, but the urban ore deposit has the advantage of being already in granular form, in contrast with the natural ore deposit that may require lengthy and expensive processing in order to reach the overburden and concentrate the ore from the gangue. However, to dissolve vitrified MSWI residues is a very difficult task requiring highly aggressive chemical conditions using strong acids. We think that low-temperature pre-concentration steps even under high pH conditions (since the residues have strongly basic pH) can be explored as an alternative extraction route in order to upgrade the REE contents from the starting urban ore.
Conclusions and outlook

Bottom and fly ashes from MSWI have an average concentration of 103 and 54 mg/kg ΣREY, respectively. Mass flow analyses indicate that the expected annual flow is 1.1 t/a LREE and 0.3 t/a HREE, whereas for bottom ashes is 22.5 t/a LREE and 5.2 t/a HREE. Therefore MSWI residues might represent a low concentration stream of REE. The independent sample t-test reveals that REE flows in FA and bulk MSWI residues (BA+FA) are statistically equal for the two incinerators, while the estimation of REE flows in BA differ from the two plants. Major elements like P2O5 and Al2O3 show a positive correlation with REE and also magnetic susceptibility values can be used as proxies for REE occurrence, although magnetic data still remains to be understood and other magnetic properties of MSWI residues should be investigated.

References
