# THE ROLE OF HYDROMETALLURGY IN THE PRODUCTION OF THE CRITICAL METALS

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## Abstract

Critical materials (Platinum group, Rare earth elements, Ge, Ga, In,.) represent some metals having a big importance for the future of the economy in the European countries. It is very difficult to replace these critical metals by other metals. Because of the high application, the demands of these metals are increased, but the production can not follow its increased consumption in electronics, catalysis and medicine. The EU Raw materials Initiative in 2010 has reported a list of critical raw materials (totally 41) in European countries. The 14 elements as rare earth elements belong to critical materials. The future use of rare earth elements (lanthanum, yttrium, cerium,..) is expected to be increased in the European countries. The selective production of rare earth elements is the most important aim in the processing of raw materials. The hydrometallurgical treatment (dissolution of minerals under an atmospheric and high pressure, purification of solution through solvent extraction and fractional crystalization, filtration, precipitation and chemical reduction from solution) was mostly applied for the selective metal production from ores and secondary materials. The use of ionic liquids s solvent is the newest way in order to improve dissolution of critical metals. Hydrometallurgical treatment makes possible to limit the environmental impacts like residual waste producing, energetic expenditure and reagent consumption. Hydrometallurgy offers also an alternative to most used pyrometallurgical treatment. Although a pyrometallurgical treatment at higher temperatures is an efficient technique to recover some metals (copper, precious metals) from electronic waste, this treatment but does not allow the recovery of critical metals like gallium and rare earths that are lost during the process. The role of hydrometallurgy in the production of the critical metals shall be presented in this work.

## Introduction

Natural resources, including raw materials like minerals and metals, have a big importance for the European and global economy and inescapably govern the quality of modern life in each society. Taking into account global population increase and economic growth of developing and emerging countries, EU predicts that the pressures and risks on securing vital raw material resources for EU industries are increasing as a response to this, EU launched in 2009 the EU Raw

Materials Initiative which concluded already in ranking 41 mineral and metals as "critical" for EU based on their economic importance for the EU industry as well as their predicted supply risk (Antimony, beryllium, cobalt, fluorspar, gallium, germanium, graphite, indium, magnesium, niobium, platinum group metals, rare earths, tantalum, tungsten) [1]. Amongst these critical materials and with the highest score in supply risk, are listed the Rare Earth containing 14 elements (yttrium, scandium, and so called lanthanides: lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium).

*Table 1: List of critical raw material and selected emerging technologies [1]*

| **Raw material** | **Emerging technologies (selected)** |
|---|---|
| Antimony | Micro capacitors |
| Cobalt | Lithium-ion batteries, synthetic fuels |
| Gallium | Thin layer photovoltaics |
| Germanium | Fibre optic cable |
| Indium | Displays, thin layer photovoltaics |
| Platinum, palladium | Catalysts |
| Niobium | Microcapacitors, ferroalloys |
| Neodymium | Permanent magnets, laser technology |
| Tantalum | Micro capacitors, medical technology |

Demand from emerging technologies and critical metals in 2030 is dramatically higher (as shown in Table 2)

*Table 2: Global demand of the technologies/ raw materials of critical metals [1]*

| **Raw material** | **Production in 2006 (t)** | **Demand from emerging technologies 2006 (t)** | **Demand from emerging technologies in 2030 (t)** |
|---|---|---|---|
| Ga | 152 | 28 | 603 |
| In | 581 | 234 | 1.911 |
| Ge | 100 | 28 | 220 |
| Nd (REE) | 16.800 | 4.000 | 27.900 |
| Pt (PGM) | 255 | very small | 345 |
| Ta | 1.384 | 551 | 1.410 |
| Ag | 19.051 | 5.342 | 15.823 |
| Co | 62.279 | 12.820 | 26.860 |
| Pd (PGM) | 267 | 23 | 77 |
| Ti | 7.211.000 2) | 15.397 | 58.148 |
| Cu | 15.093.000 | 1.410.000 | 3.696.070 |

This category of raw materials, which the EU Raw Materials Initiative has labelled "critical" due to both their technological importance in the European industry and their high supply risk, as their primary production is based in a handful of countries, like China (antimony, fluorospar, gallium, germanium, graphite, indium, magnesium, rare earth, tungsten), Russia (PGM: platinum, palladium, iridium, rhodium, ruthenium, osmium), Republic of Congo (cobalt, tantalum) and Brazil (niobium und tantalum), rendering EU 100% import depended. Among these raw materials are the so called "Critical Metals (CM)", small amounts or traces of which are used in numerous high-tech electronic, automotive and industrial applications [2]. With 8 to 9 million tons of electronic waste arising across the twenty seven members of the European Union in 2009, closing the loop for electronic and electrical devices would lead to the elimination of significant environmental problems and a create a sustainable source for critical metals in EU.

*Figure 1: Average critical and precious metal concentration per high tech electronic device*

Similarly to electronic waste, recycling spent automotive catalyst converters is valuable source of critical metals and namely of Platinum Group Metals (PGMs) and Rare Earth Elements (REEs). Environmentally processing 2 tons of the used auto catalytic converters can avoid mining 150 kg of ores and all the following stages which are necessary to obtain pure metal PGMs. Today it is estimated that almost 30 % of all PGM ever mined have been used for auto catalytic converters and more than 2,000 tons of these is still globally "on the road" [2]

## Rare Earth Elements (REE)

Rare Earth Elements (REE) is the collective name for the elements samarium, yttrium, lanthanum and the 14 elements following lanthanum in the periodic table (the so called lanthanides). They occur mainly in minerals like bastnaesite and monazite, and can only be mined collectively. Due their chemical similarities and high chemical activities REE extraction is very difficult to achieve and requires intense processing conditions, while REE separation is practiced through multiple processing cycles. The REE and their compounds (oxides and chlorides) are used in numerous areas of industry for a wide range of purposes, including metallurgy, catalysts in the chemical industry, colouring of glass/ceramics, production of magnets, phosphors and batteries. Additionally they are vital elements in emerging technologies like Solid State Fuel Cells, Superconductors and high performance magnets.

Currently China controls one third of REE world reserves and has monopolized the global market of REE production as in 2009 it produced 97% of global consumption. In light of stockpiling practices and export taxes currently employed by China, REE prices have risen, while concerns for possible restrictions or even ban of Chinese REE exports exists. With numerous European industries heavily depended on REE raw materials, EU must secure a viable current and future supply of REE minerals as well as develop from the ground up the currently non-existent European REE extraction and processing industry.

## REE extraction and refining technologies

All existing REE extraction technologies while custom developed for processing specific ore concentrates, follow in general three steps: (i) ***REE ore chemical treatment***, where REE are retrieved collectively from the ore concentrates, (ii) ***REE separation*** into separate industrial REE compounds (oxides, chlorides, etc) and ***REE metal production***, in the cases where REE metals are required. The general outline of developed REE extraction processes is given in figure 2.

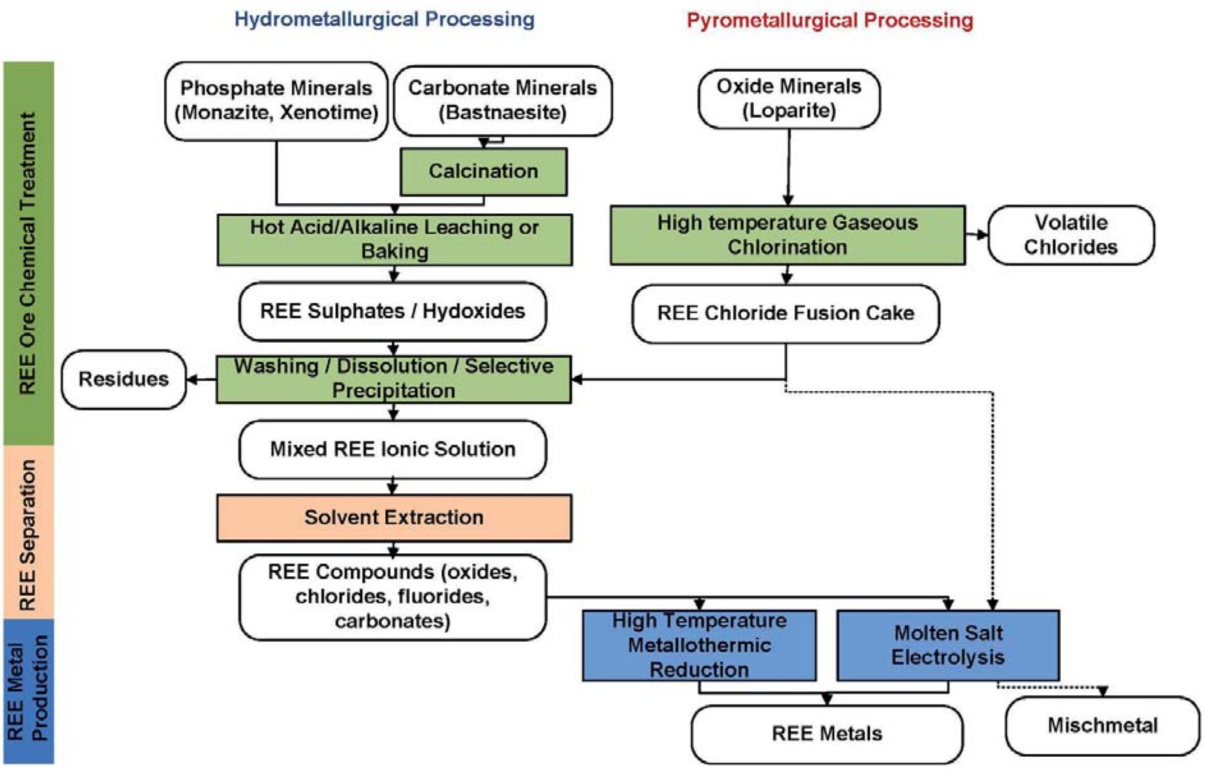

*Figure 2: The most used technology for the winning of REE and their alloys*

Developed **REE ore chemical treatment processes** differ significantly, depending on the type of ore processed. Phosphate and carbonate REE minerals follow hydrometallurgical processing, while oxide minerals follow pyrometallurgical processing.

**Hydrometallurgical processing** for phosphate minerals, like monazite ($(Ln,Th)PO_4$) and xenotime ($YPO_4$), begins with pressurized hot leaching with mineral acids or sodium hydroxide, in order to break the mineral's crystal lattice and convert REE in soluble compounds, like sulphates or hydroxides. Carbonate minerals, like bastnaesite ($LnCO_3F$) are subjected first or in parallel in a heat treatment (calcination or baking with sulphuric acid), in order to assist decomposition of carbonates and fluorine gas removal [2]. The initial ore leaching stage is succeeded by a washing/dissolution/selective precipitation stage, whereby ore residues (including radioactive thorium oxides, where present) are removed and an ionic solution, containing only REE ions, is produced.

**Pyrometallurgical processing** is followed in the cases of oxide minerals like loparite ($(Ln,Na,Ca)(Ti,Nb)O_3$), where gaseous chlorination at high temperature (1000- 1200$^oC$) in the presence of reducing agents (carbon) is used [3]. The more volatile chlorides of titanium, niobium, and tantalum are separated from the less volatile chlorides of REEs and other elements, which remain as a fusion cake. This fusion cake of REE chlorides can be dissolved in sulphuric acid yielding an REE ionic solution or it can be treated directly by molten salt electrolysis to produce cerium mischmetal [4]

The ***REE separation*** from mixed ionic solutions poses one of the most difficult problems in inorganic chemistry [4], due to their chemical similarity. Fractional crystallization and ion-exchange techniques are used to separate them in small amounts but commercial separation generally is achieved using liquid–liquid solvent extraction [5]. This process consists of addition of a solvent composed of a mixture of organic compounds to the pregnant aqueous solution in a series of mixing/settling cells that allow repetitive fractionation during a more-or-less continuously flowing process. Following precipitation and drying, specific REE compounds (usually oxides) with purities in excess of 99.99% can be produced by such process.

The ***REE metal production,*** due to REE's highly electropositive character, is currently achieved through molten salt electrolysis of REE chloride and fluoride salts or through high temperature (1000-1300$^0C$) metallothermic reduction of REE oxides or salts from alkali metals, alkaline earth metals or aluminium [4]. Thus, the current state-of-the-art processes for REE extraction follows complicated, energy and resource intensive technologies, such as pressurized leaching at elevated temperatures with large acids consumption (and therefore large acid waste water production) , as well as multi-staged solvent extraction. Some simplified hydrometallurgical scheme for the production of metal from some ore via prepared concentrate after beneficiation was presented at Figure 3:

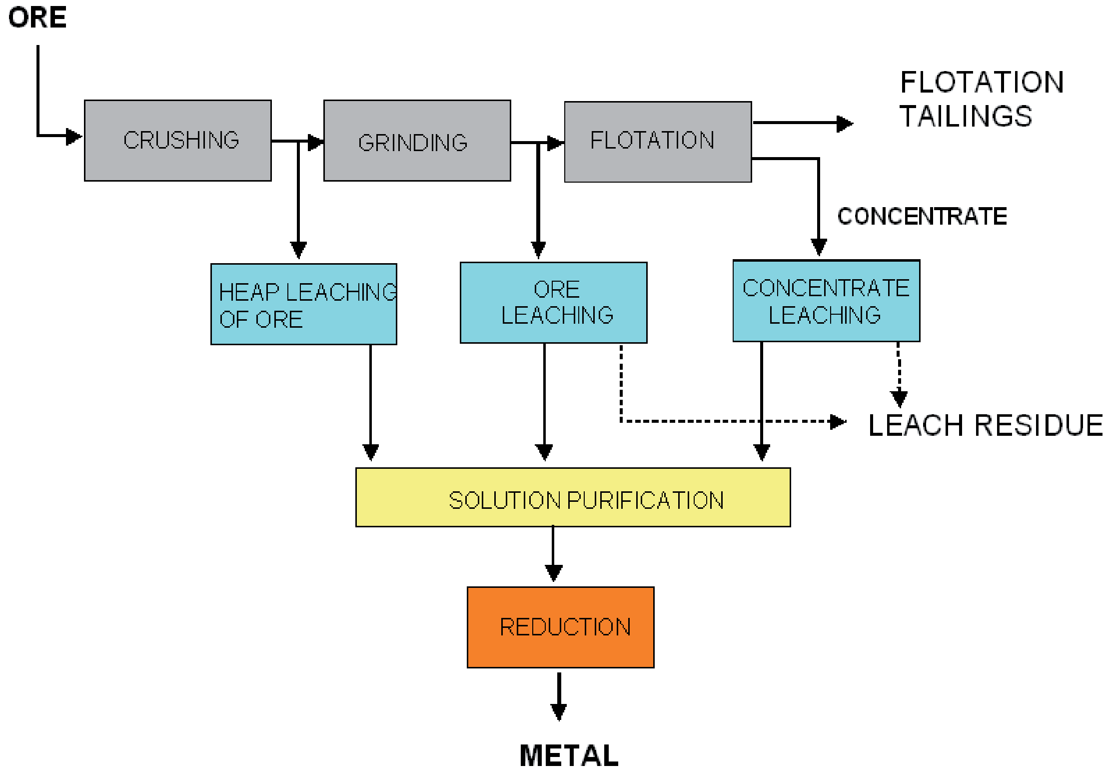

*Figure 3: From ore to metal using hydrometallurgical process [6]*

## Conclusion

The EU Raw materials Initiative was identified a list of 41 critical raw materials at the EU level in order to solve this problem in the future. Especially rare earth elements REE (14 elements) belong to critical materials for the economy of the European countries in the next twenty years. The future application of REEs is expected to be increased in the European countries. Regarding an environmental protection some selective winning of rare earth elements and their alloys via hydrometallurgical represents the most important aim in the processing of raw materials. Developed REE ore chemical treatment processes differ significantly, depending on the type of ore processed. Phosphate and carbonate REE minerals shall be treated by hydrometallurgical processing, while oxide minerals follow pyrometallurgical processing.

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