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ENVIRONMENTAL DEFECTS AND ECONOMIC IMPACT ON GLOBAL MARKET OF RARE EARTH METALS

G Charalampides, K Vatalis, V Karayannis and A Baklavaridis

Department of Environmental Engineering, Technological Education Institute of Western Macedonia, 50100, Kozani, Greece

E-mail: chara@teiwm.gr

Abstract. Rare earth elements include the 14 lanthanides as well as lanthanium and often yttrium. Actually, most of them are not very rare and occur widely dispersed in a variety of rocks. Rare earth metals are vital to some of the world's faster growing industries: catalysts, Nd-magnets, ceramics, glass, metallurgy, battery alloys, electronics and phosphors. Worldwide, the main countries for distribution of rare earths deposits include China, USA, Russia, Brasil, India, Australia, Greenland and Malaysia. The mining and processing of rare earth metals usually result in significant environmental defects. Many deposits are associated with high concentrations of radioactive elements such as uranium and thorium, which requires separate treatment and disposal. The accumulation of rare earth elements in soils has occurred due to pollution caused by the exploitation of rare earth resources and the wide use of rare earths as fertilizers in agriculture. This accumulation has a toxic effect on the soil microfauna community. However, there are large differences in market prices due to the degree of purity determined by the specifications in the applications. The main focus of this article is to overview Rare Earth Metals' overall impact on global economy and their environmental defects on soils during processing techniques and as they are used as fertilizers.

1. Introduction

The term 'rare earths' is misleading, as it does not refer to their abundance in the earth's crust, but to the inconspicuous appearance of the minerals from which they were originally isolated. Almost all rare earth elements (REE) in the earth's crust are more abundant than gold, silver or platinum, while Cerium (Ce) is the most abundant of all REEs and is more common in the Earth's crust than copper or lead. Admittedly, rare earths are not present in equal amounts in REE ores. They are generally divided into the light rare earth elements (LREEs) and the heavy rare earth elements (HREEs), with the HREEs being much less abundant and thus much more valuable. The attributions to these groups are not distinct, but in general Lanthanum to Gadolinium are called LREEs while Terbium to Lutetium are called HREEs.

Despite their similar basic chemical properties, each REE displays unique characteristics for specific applications and usually cannot be substituted one for another. This has resulted in a 'criticality' classification which is based on a REE importance for specific applications (e.g. renewable energy), lack of comparable and reliable substitutes, and the monopolization of supply sources. According to the U.S. Department of Energy, the group of critical REEs comprises five elements: neodymium, europium, terbium, dysprosium, and yttrium [1].

REEs have gained visibility to the general public through the crisis of 2010 and the price spike of 2011 [2]. Numerous headlines about REEs have appeared in the media, and suddenly the world became alarmed that China was about to crush high-tech industries of Western economies due to imposition of export restrictions. China at that time was holding a share of 95 per cent of global production of REEs. There are fewer than twenty large companies that trade REEs, and these are distributed to a handful of countries: China, Canada, Australia, USA, Russia, India and Japan. China is the biggest supplier of REEs in the world, while United States, Japan and Germany are the biggest importers [3].

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The REEs are found, usually several together, in a variety of accessory minerals, such as phosphates, carbonates, fluorides and silicates. They rarely form more continuous ore bodies.

REEs do not occur as native elemental metals in nature, only as part of the host mineral's chemistry. For this reason, the recovery of REMs must be accomplished through complex processing methods to chemically break down the minerals containing the REEs.

Despite the abundance of more than 200 known REE-bearing minerals, only three of them are considered to be the principal REE mineral ores most feasible for the extraction of REMs: bastnäsite [(Ce,La)(CO_3)F], xenotime (YPO_4), and monazite [(Ce,La)PO_4)] [4].

Rare earth elements (REEs) have previously been used as geochemical tracers in groundwater flow systems owing to the commonly reported similarities between their input-normalized REE patterns and those of the aquifer rocks/sediments through which they flow and react [5,6].

REEs have been used in fertilizers in the agriculture of China for about 20 years. They have been shown to be beneficial elements for plants. For example, they have improved the yield and quality for several kinds of crops. Although they are widely distributed geographically, they are chiefly mined, concentrated, and separated in China, which holds the largest reserves in the world (80%) and is a major producer of REEs for the world market. Since 1990, REE fertilizer has been widely used in more than 20 Chinese provinces [7].

This paper reviews the current literature on environmental impact of REMs after mining, processing and disposal, mainly due to high concentrations of radioactive elements such as uranium and thorium, as well as their use as fertilizers in agriculture. It also studies in brief their economic impact on global market.

2. Environmental defects deriving from processing and soil applications of REMs

REEs may possibly also be extracted from alternative sources, such as industrial wastes, and by recycling end-of-life REM-bearing products such as consumer products or lighting. Substitution especially of the less common REEs is another important option. An entirely different but equally relevant issue concerns the environmental impact of REE mining and beneficiation. Of particular concern is the common association of REE with thorium and uranium and thus the need to strictly control the dispersion of radioactive elements into the environment [8]. This pertains in particular to the treatment and disposal of tailings. Rather lax legislation in China has resulted in significant pollution, especially related to illegal mining [9].

2.1. Processing techniques

The REE processing is characterized by high levels of water consumption, energy inputs, and chemicals use [10]. The land allocation can be also significant for both mining and processing operations, as well as for the tailings dams, and long-term storages of the radioactive waste materials.

The method of physical beneficiation of rare earth bearing minerals depends on the mineralogy of the deposit. In most cases, the deposits are presented as hard rock, requiring the ore to be initially comminuted to liberate the valuable mineral grains [11].

Conventional physical separation methods such as gravity separation, magnetic separation, electrostatic separation and froth flotation are employed to concentrate rare earth bearing minerals [12]. In placer, mineral sands deposits, gravity separation (spirals) is typically used to remove the silicate gangue and multiple magnetic and electrostatic separation stages progressively concentrate the monazite from the other heavy minerals-ilmenite, rutile, zircon and leucoxene. Due to their nature, ion-adsorption clays require no physical beneficiation and can be processed by direct hydro-metallurgical techniques [13].

The concentration of pure REEs from mined rock is complex, involves many stages, and impacts the economic decisions of the industry. First, the rare earth containing minerals are recovered from the host rock via comminution and physical separation. The concentrated minerals are subsequently chemically leached into a solution in a process commonly referred to as cracking. The individual elements are selectively removed from the mixed REE solution via hydrometallurgical techniques such as solvent extraction and ion exchange. The precipitated products can either be sold as pure metal oxides or reduced to pure metal products depending on the required end purpose (Figure 1).

Figure 1. Schematic of REE production technology [11].

The development of recycling and reuse of REEs from waste materials or mine tailings is generally recognized as a more environmentally friendly activity than establishing a new REE mine [14]. However, recycling techniques for REEs have a number of environmental consequences including high energy use, consumption of large amounts of chemicals and the generation of waste chemicals and water. Hydrometallurgical methods to recycle REE magnets require large amounts of strong mineral acids and non-recyclable reagents such as H_2SO_4, NaOH and HF, and generate large quantities of waste water [14].

3.2 Environmental Degradation due to radioactivity of REMs

Most of the rare earth deposits have the presence of radioactive thorium and in some cases uranium. The concentration of radioactive elements, usually being relatively benign for human health in the ore body, rises significantly during beneficiation. This could be of serious concern for the waste by-product, emissions or tailings after the cracking stage in the processing of rare earths bearing minerals [15].

The concentration of thorium and uranium varies significantly for different ore bodies. Intermediate concentrates and final waste products contain radioactive elements depending on the processing route and potential co-extraction of Th/U. A higher concentration of thorium/uranium in the ore body makes the co-production of radioactive elements more feasible. However, the current market for thorium is very limited [16] and most of it has to end up either at the long-term storage or permanent disposal. The separation, treatment and disposal of radioactive materials in the latter case would result in significant additional costs, as well as high human health and environmental risks. The low radioactive ore bodies are highly preferable for the new REE projects, but even in this case there are environmental issues that have to be carefully addressed.

It is likely that the radioactivity aspect is overlooked in many new REE project proposals, both from the environmental and human health risk perspectives, and from the economic point of view (i.e. costs associated with treatment, disposal, and future land rehabilitation). Nevertheless, China has banned mining of pure monazite due to high-level radioactive elements and recently revised emission guidelines for the rare earths industry, setting standards that are in some cases more stringent than industrial nations [16]. Global awareness of these developments suggests that new REE projects in other jurisdictions may require revision of radioactive waste management before they can successfully go into production.

3.3. Soil defection by using REEs as fertilizers

Recently, the environmental pollution of rare earth elements (REE) has increased dramatically as a result of wide application of REEs in agricultural production as microelement fertilizers as well as in industry. Therefore, the biogeochemical cycling of REEs and their ecological and environmental effects are greatly concerned by many researchers. Rock weathering is an important REE source for an ecological system and a key process of global biogeochemical cycling of REE [17]. REE enrichment characteristics and mechanism analysis reveal that the released REE from weathering of carbonate soil pollution, and rocks (mainly limestone), sillicalite and shale are mainly stored in profiles.

In addition to their use in industry, REEs are more widely applied to cropland as microelement fertilizers due to their abilities to increase yields and improve qualities of crops. As a result, more and more REEs are moving into the ecosystems. They accumulate in soils, bioaccumulate in crops, and enter the food chain, causing a problem of REE environmental pollution special to China. In recent years, REE environmental effects have become of great concern [18]. Some work should be done to and a method should be developed that can reliably estimate bioavailability of REEs to plants and thereby evaluate the potential health risk of REEs in soils and predict their impact on the ecosystem.

Mixtures of REEs in fertilisers are nowadays widely used in Chinese agriculture to improve crop nutrition, and have been in common use for about 20 years [19]. In most cases, however, La, several lanthanides, and probably Y are contained in the mixtures, making it difficult to conclude whether any single element is of particular importance or whether the effects are less element-specific, which seems most likely. The capacity of rare earth uptake by the roots might be limited, mainly due to the self-protection mechanisms of the plants against adverse effects of rare earths [20]. The results of several studies [20, 21] showed that the accumulation of REEs in soil was significant in the study area and its concentration was strongly correlated with the distance from the pollution source.

Gillet and Ponge [22] have indicated that soil fauna is very sensitive to the changes in the soil environment. The soil fauna community responds to soil degradation and soil heavy metals pollution, such as Cd, Cu, Pb and Hg, in many ways. Thus, soil fauna can be an indicator of soil degradation and is often used to evaluate soil quality.

Heavy metal pollution of soil can lead the soil fauna community to change, but the response of different soil fauna to contamination is different. Almost all the deposits of REE contain the radioactive element thorium, and therefore environmental cost should be related to market competitive force.

3. Economic Impact On Global Market

The balance of demand and supply in the world market of REMEs was always rather unstable. After a rapid increase in demand in the 1980s by developed countries, it somewhat decreased in 1991–1993. In that moment, the REMs market was affected, first, by a tremendous increase in their production in China and, second, by the presence of large reserves in countries of the former Soviet Union [23].

The most significant increase of prices took place during the years 2009-2011 as it is shown by the Table 1. More recently (2012), according to the Metal-Pages quotations [24], there was a sudden and substantial fall in prices. These changes of trend are likely due to different reasons: the actual, persistent heavy economic crisis of the industrialized countries; the contraction of hi-tech consumption; the placing on the market of large stocks of REOs by some Chinese private operators fearful of possible inspections and confiscations by the Chinese Government [25].

REEs	2009	2010	2011	2012	Price fall from 2011 to 2012 (in %)
Ce	4,5	61	158	42,5	73
La	6,25	60	151,5	36	76
Pr	14	86,5	248,5	175	30
Nd	14	87	318	154	52
Dy	100	295	2510	1500	40
Eu	450	630	5870	4010	32
Tb	350	605	4410	3400	23

Table 1: Prices of REEs (in US$/kg) for the four-years period 2009 – 2012, showing a significant increase between 2009-2011, and thereafter a sudden and substantial fall for 2012, with the corresponding percentage lost (data based on Metalpages Inc., [24]).

Germany has already made diplomatic efforts to secure a diversified supply of REEs, including with other resource rich countries such as Australia [26, 27]. Countries such as China and India "have now given a strategic orientation to their raw materials policies and have taken measures to meet their needs for raw materials", and that "in the medium term, this can impact on German and European companies' access to sources of raw materials" [28].

In Greece significant reserves of rare earth elements are found in alluvial deposits in the coastal and groundwater environment of Strymona gulf between Strymona river and Kavala region, Northern Greece. Specific ore deposits research estimates ore reserves of 485 million t with an average content of 1.7% rare earths. Detailed and systematic investigations also show that bauxites and lateritic bauxites in

Central Greece contain representative concentrations, ranging overall from 3,275-6,378 g/t REE. It must be stressed that there is still an emerging interest for the red mud from the aluminum metallurgy [29]. Generally, in Greece they occur in a number of environments and are found in igneous (primary types), sedimentary, or metamorphic rocks (secondary types) of different ages. In secondary rocks the REE have been further concentrated from a primary enrichment through sedimentary processes or weathering. Secondary types are economically the most important types in Greece [30].

4. Conclusions

Due to high demand and limited availability of REEs, Europe is unable to meet today its industrial needs for the manufacturing sector. Therefore the EU has included them in the group of 14 critical minerals. Namely, China currently controls completely the mining activity (almost 95% of world production) and thereafter the production, the enrichment technologies and metallurgy and end-metal products of rare earths, resulting for both Europe and the U.S.A. in full industrial dependency, reaching almost to 100 %. This is happening at a time when the demand and needs tend globally constantly growing at an annual rate of 8-11%. However, Canada and Australia, for example are currently running significant mining projects to enter production in 2019, while in Sweden there are plans to begin production in 2018. Also, Greenland holds some interesting exploration projects which are in early exploration stage. Almost 50,000 tons of rare earths are needed per year out of China at present time. With a rate of 15% demand increase, then in 2018, the total demand out of China should be at least 100,000 tons on the basis of the world economy continuous increase.

There are large differences in market prices of rare earth oxides. Also, the prices depend on the degree of purity determined by the specifications in the applications. The price ranges from 11 $/kg La_2O_3 to 1,600 $/kg Eu_2O_3 [31]. It has to be underlined however, that China controls 95% of world production.

The distribution of metals in the aerial parts of plants is the result of both the fixation and the transfer mechanisms. The complexation of organic ligands in the xylem vessels plays an important role, and elements with strong complexation capacities (strong motilities) are preferentially transported to the top. The REEs concentrations, as well as total nitrogen, total potassium, and pH, had some effect on the soil macrofauna community. A small amount of REEs can promote soil macrofauna diversity, but a large amount of REEs can reduce the soil macrofauna diversity.

In order to fully understand the effects of REEs in agricultural application, environment and human health, it is suggested that future research in several areas is needed, which would shed new light on the effects of REEs on agriculture, environment and human health.

Finally, it has to be emphasized that environmental concerns must be paid attention; almost all the deposits contain the radioactive element thorium. Environmental cost is related to the market competitive force. It is very important that current rare earth market with profitable prices is greatly stimulated by the strict quota control of China and curb of smuggling to limit the supply. Therefore, all producers should pay great attention on the adjustment of future quota amount [32].

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