



Extraction and separation of rare earth elements from hydrothermal metalliferous sediments

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ABSTRACT

Rare earth elements (REE) can be efficiently extracted from umbers, ferromanganese metalliferous sediments of the Troodos ophiolite (Cyprus) by simple leaching and selective precipitation, without accumulation of radioactive by-products. Umbers are dominantly composed of amorphous Fe and Mn oxides with minor goethite, quartz and zeolites, and contain 350–500 mg kg⁻¹ of rare earth elements and yttrium (REY), 200 times lower than many of the major REY source ores. To compensate for relatively low grades, a cost-effective extraction process was developed that utilises a weak lixiviant concentration (0.1–1.5 N) and short reaction times (5 min to 11 h). Acid solutions recover 70–85% of the initial sample REY content even at 20 °C. By contrast, extraction using ionic solutions of NaCl and ammonium sulphate proved ineffective. Acid recoveries of REY increase by nearly 10% at 70 °C and the use of different acids (HCl, HNO₃, H₂SO₄) yields comparable results. The main impurities in the leachate include Ca and Na at even the weakest acid concentration (0.1 N). However, two-step leaching method greatly reduces concentrations of impurities in the REY-rich liquor, although with REY losses approaching 20%. Purification of the leach liquor via selective precipitation of REY as an oxalate is highly efficient although pH dependent. With maximum REY precipitation (96–99%) occurring between pH 1 and 2, the precise adjustment of pH allows separation of REY from other precipitating impurities (Ca). The maximum purity of the precipitate is achieved at pH 1.1 (> 65%). Strong and consistent fractionation along the lanthanide series observed during the precipitation experiments has been successfully explained using a speciation modelling software (PHREEQC). The uptake of REY by oxalate in the experiments closely follows the bell-shape distribution of REY-oxalate solid complexes stability constant ($-\log \beta(\text{RE}_2\text{Ox}_3\text{nH}_2\text{O})$) replicating the fractionation trends observed at pH < 1.1. In addition, the modelling demonstrates that at equivalent REE concentration in solution, oxalate precipitates fractionate REY in the following order: middle REE > light REE ≫ heavy REE. This ordering and the variable degrees of uptake reflects the interplay of aqueous REY-oxalate complexes ($\log_{\text{H}_2\text{O}}\beta_1$, $\text{Ox}\beta_1$ and $\text{Ox}\beta_2$) with the natural fractionation induced by solid REY-oxalate stability constant distribution. Overall, the combined leaching process and selective oxalate precipitation produces a total enrichment factor ranging between 1400 and 2400 for REY from the sample to the oxalate precipitate in a simple two-step process forming a high-purity end-product of mixed REY.

1. Introduction

The perceived supply risk for essential materials used in the development of green energy and other state-of-the art technologies provides motivation to investigate new sources for these raw materials. Many are characterized as “critical”, given supply risks posed by geographic location, the economic and political stability of producing

countries, limited possibilities for substitution and currently low-levels of recycling (European Commission, 2014; Graedel et al., 2014). At present, 20 raw materials are listed by the European Union as critical. Among these critical elements, the lanthanides and yttrium (REY) form a group of 15 metals (Rollat et al., 2016) essential for the development of applications in the low-carbon energy sector (magnets, low-energy lighting, wind turbines, batteries), industry (catalysis, alloys, oil

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refining), and other technologies (lasers, optics) (Guyonnet et al., 2015). More than 90% of REY produced worldwide in the last twenty years originated in China, a near monopoly that reflects environmental and economic factors rather than the unequal distribution of REY resources across the world (Weng et al., 2015). Indeed, large primary deposits are known outside China including more than 550 carbonates/alkaline complexes worldwide (Kanazawa and Kamitani, 2006; Chakhmouradian and Wall, 2012; Jordens et al., 2013; Jaireth et al., 2014; Xie et al., 2014; Hoshino et al., 2016).

Solvent extraction constitutes the most common treatment of REE-bearing minerals, such as xenotime (YPO₄), bastnäsite ((Ce,La)CO₃F) and monazite ((REE,Th)PO₄) ores, following energy-consuming beneficiation via gravity separation, desliming, magnetic or electrostatic separation and froth flotation (Jordens et al., 2013; Kumar et al., 2014; Xie et al., 2014). The hydrometallurgical process uses strong acid or alkali leaches (sulphuric acid and sodium hydroxide being the most common) at temperatures of 200–400 °C, in a process commonly referred to as cracking (Habashi, 2013; Golev et al., 2014). This treatment produces REE-rich leach liquors usually in the range of 1–40 g L⁻¹ RE₂O₃ with small amounts of impurities (Chi et al., 1995; Abreu and Morais, 2010). REY are separated from co-leached elements by further treatment such as solvent extraction and ion exchange using selective precipitation as carbonates or oxalates by pH adjustment. Rare earth oxalates and carbonates are then roasted to form a mixed RE oxide product ready for sale as a RE alloy known as mischmetal, sent to specialized factories for further separation treatment into individual high purity RE oxides or reduced to pure metal products depending on the required end use (Christie et al., 1998; Golev et al., 2014). The separation of a mixed product into individual elements is inherently difficult due to their very similar chemical behaviour. Multiple methods exist such as selective oxidation/reduction, fractional crystallisation-precipitation, and ion-exchange, though the most effective approach is solvent extraction using organophosphorus compounds (e.g., EDPA, HDEHP, EHEHPA, or TBP) (Abreu and Morais, 2014; Kumar et al., 2014; Xie et al., 2014). All these methods are energy- and material-consuming as they require multiple iterations to obtain a high purity individual rare earth oxides (REO) (Abreu and Morais, 2014).

Another problem associated with REY production is the handling of radioactive waste as most REY-rich primary magmatic deposits possess high concentrations of actinides; monazite contains 4–12 wt% Th and although U concentrations are generally low, anomalous content of up to 14 wt% can occur (Jordens et al., 2013). Uranium and thorium are both concentrated during the beneficiation of REY and the tailings wastes may exhibit high levels of radioactivity after cracking. Co-production of radioactive elements is feasible for the highest U-Th concentration ores, albeit with significant additional costs (Golev et al., 2014). These issues have led to notable pollution in China and Malaysia (Golev et al., 2014; Kolo et al., 2015). For many sites, industrial processing is followed by costly remediation and waste disposal in long-term storage. Significant radioactive element concentrations constitute important economical drawbacks for any new REY exploitation project.

Considering the problems associated with magmatic-related REY deposits and despite their abundance, alternative sources of REE more readily beneficiated with low radioactive waste are attracting attention alongside efforts to increase recycling of REY from scrap or end-of-life consumer products. The abundance of neodymium-iron-boron magnets (NdFeB) in cell phones, hard drives and wind turbines forms the major target for this recycling effort with promising results on Nd recovery in the laboratory (Vander Hoogerstraete et al., 2014). In addition, development of REY production from industrial waste or by-products such as red-mud (Ochsenkühn-Petropulu et al., 1996; Tsakanika et al., 2004; Qu and Lian, 2013; Liu and Naidu, 2014; Borra et al., 2015; Deady et al., 2016) and coal residue (Rozelle et al., 2016a) has received considerable interest. These formations contain REY-bearing minerals and/or adsorbed REY that are transferred to the wastes during initial ore processing. These wastes constitute a low-grade resource with

economically significant tonnage due to the importance and spread of the coal and aluminium industries (Goodenough et al., 2016). Other alternative sources, include sea-floor deposits such as ferromanganese nodules (Fujimoto et al., 2016), hydrogenetic crusts, and marine clays (Kato et al., 2011; Menendez et al., 2017) that can have significant REY concentrations (Hein et al., 2013). Although of scientific interest, their relative inaccessibility and need for advanced mining technologies makes their economic exploitation challenging. As an initial approach to establish methods for REY-extraction from such marine formations, here we investigate sub-aerial equivalents of these deposits preserved in ophiolites; slices of ancient oceanic crust now present on-land that provide ease of access and sampling. Given that, the ferromanganese metalliferous sediments of the Troodos ophiolite in Cyprus known as umbers constitute an obvious best choice for study. These deposits represent direct analogue of actual oceanic metalliferous sediments formed in the vicinity of hydrothermal vents (Boyle and Robertson, 1984; Richards and Boyle, 1986, 1990; Robertson and Varnavas, 1993a), and have been exploited since classical times for pigments. Nevertheless, to our knowledge no previous work has investigated the processing of these deposits as a potential source of REY.

This study investigates the potential recovery of REY from umbers, metalliferous sediments of the Troodos massif in Cyprus, as analogue to numerous oxide-based deposits found on-land that may provide an alternative to magmatic-related REY deposits that currently dominate global supply. Herein, we report the influence of various kinetic parameters such as the nature and concentration of lixiviant, reaction times, temperature and pulp density, on the release of REY during simple and sequential leaching experiments. We also explore in detail the efficiency of oxalate precipitation for the selective extraction of low concentration REY from other impurities present in the leach liquor via pH-dependent experiment and geochemical modelling.

2. Background geology

Umbur deposits constitute the basal facies of the sedimentary sequence that accumulated above the extrusive lavas of the Troodos ophiolitic massif, Cyprus. These metalliferous formations resulted from the precipitation and accumulation on the paleo seafloor of Fe and Mn oxides from high temperature hydrothermal solutions in the Tethyan Ocean 91 million years ago (Robertson and Hudson, 1972; Boyle, 1990). Umbers are found interstratified with or overlying the Upper Pillow Lavas of the Troodos ophiolite as lenticular bodies or in shallow depressions of the lava surface. Although there are minor accumulations at multiple levels within the lavas, supra-lava umbers are by far the most abundant and these constitute the basal facies of the Perapedhi Formation, bracketed between the basaltic upper pillow lavas and radiolarian cherts of Campanian age (Robertson and Hudson, 1974). Massive umbur deposits can reach thicknesses of 4 m, although most are limited to 1 m. However, records indicate that outcrops up to 35 m thick existed prior to extensive extraction in the Mangaleni quarry (Boyle, 1984) where production peaked at 6000 t y⁻¹ (Morse and Stevens, 1979, Cyprus Geological Survey, 2006). The lateral extent of umbur deposits is predominantly controlled by the initial sea floor topography, subsequent preservation from sea floor weathering and more recent anthropogenic activity since Classical to the modern era.

Umbers comprise brown Fe-Mn-rich mudstones with an amorphous oxyhydroxides-dominated mineralogy, formed by the accumulation of hydrothermal plume fall-out of Fe-Mn oxyhydroxides (Boyle, 1990). Umbur deposits are commonly carbonate-free. Dissolved Fe and Mn from the effluent issued at hydrothermal vents oxidize in contact with bottom seawater to form colloids with strong surface charge that enables the efficient scavenging of dissolved species (Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003). Umbers thus acquired seawater-like REE signatures with concentrations up to ~500 mg kg⁻¹ total REY (0.06% total REO (TREO) as RE₂O₃) with low concentrations of radioactive elements (average U = 2.4 mg kg⁻¹ and

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