

RECOVERY OF RARE EARTH ELEMENTS FROM HUNGARIAN RED MUD WITH COMBINED ACID LEACHING AND LIQUID-LIQUID EXTRACTION

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Abstract

The world economy is confronted with an increasing supply risk of critical raw materials. In the search for alternative sources, red mud may offer potential in particular for rare earth elements (REEs). Red mud is a by-product resulting from alumina extraction. Depending on the bauxite's origin, red mud may contain considerable amounts of REEs. The extraction of REEs from red mud by selective acid leaching was explored in this study. Hydrochloric (HCl), sulphuric (H₂SO₄) and nitric (HNO₃) acid were applied for leaching. Citric (C₆H₈O₇) and oxalic (C₂H₂O₄) acid as small molecular weight organic chelators that can be biologically produced were studied as green alternative to mineral acids. After acidic extraction, REEs were purified by liquid-liquid extraction using di-(2-ethylhexyl)phosphoric acid (D2EHPA).

Introduction

Major parts of the world economy are depending on "critical raw materials", which can be defined as materials with above average economic importance and supply risk.¹ Within the framework of the European Innovation Partnership on Raw Materials, a list of 20 critical materials was defined, including REEs.² The REEs are a collection of 17 chemical elements in the periodic table, specifically the 15 lanthanides, plus Y and Sc. One approach to lessen supply risk is the exploitation of secondary (i.e. not ore related) sources of critical materials in the frame of urban mining. Prominent secondary sources are for instance incineration ashes, demolition

waste or e-waste.¹ One of so far untapped secondary source for critical raw materials is the so called red mud, which is a residue of aluminium winning from bauxite.³ Red mud is a highly alkaline mixture with a pH usually ranging from 10 to 13 which is the result of the treatment of bauxite with sodium hydroxide, heat and pressure. Depending on the original ore extracted, it may contain considerable amounts of critical materials.⁴ Enormous quantity of red mud is generated worldwide every year. In 2014, 108 million metric tonnes of aluminium was produced worldwide.⁵ For one tonne of aluminium an approximate 1.5 tonnes of red mud is produced, reaching 161 Mt in 2014.⁶

Environmental implications

Unless managed properly, red mud may pose considerable risks to the local environment near production and deposition sites due to its alkalinity. Previously there were two main red mud disposal methods: marine discharge and lagooning on land. There is an evolution of red mud disposal strategies as there is a shift from low to high density disposal techniques i.e. from direct disposal into the sea (25–30 wt%), mud lakes (25–30 wt%), to dry stacking (45–65 wt%) and dry storage (70–80 wt%).⁷ Management of leachate water is necessary in case of the land based disposal methods due to the high risk of seepage of alkaline solution to groundwater. In this regards, it can take many years for the deposit to consolidate.⁸ The presented method of acidic leaching does not only offer critical material recovery, but also tackles problems associated with alkalinity.

Summary of techniques for rare earth elements recovery

Figure 1 shows a flow diagram on the key operations in a hydrometallurgical process to recover metals from minerals or from secondary sources like red mud. The difference is the dissolution of the secondary source or ore into the aqueous phase (leaching). In order the metal to be recovered it should be separated (e.g. by liquid-liquid extraction) and the amount of aqueous solution is reduced to generate the pure metal.

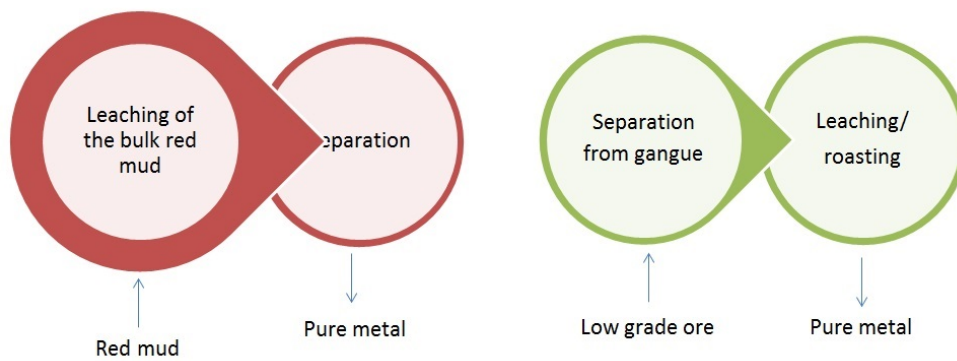


Figure 1: Summary of the key operations to recover metals from ores or from secondary sources by hydrometallurgy

Well-known hydrometallurgical processes make use of acid leaching with H_2SO_4 , HCl or HNO_3 , for instance of primary ore minerals of bastnaesite and monazite.⁹ Similarly, this is also a common method to recycle REEs from secondary sources.⁹ Few studies are available regarding acidic leaching of REEs from red mud. Ochsenkühn-Petropulu et al.¹⁰ observed that 0.5 N HNO_3 leaching (25 °C; 24 h; 50:1 L:S) recovered 80 % of Sc, 90 % of Y, 30 % of La, Ce and Pr; 50 % of Nd, Sm, Eu, Gd and 70 % of Dy, Er, Yb. According to Borra et al.¹¹ 70–80 % recovery of REEs was achieved with 6 N HCl leaching (24 h; 25 °C). One study is available for bioleaching of REEs and radioactive elements from red mud.¹² Here *Penicillium tricolor* was used in a one-step bioleaching process. The maximum leaching efficiencies of La and Ce were approx. 27 %.

After dissolution (extraction), dissolved metals are generally separated using solvent extraction, ion exchange, carbon adsorption, precipitation or ultrafiltration.¹³ Liquid-liquid is a common process to selectively concentrate metals,¹³ including REEs.^{14,15} It is based the use of two immiscible liquids, usually an organic solvent containing an extractant with the original aqueous solution containing the metal of interest. Optimally, a selective transfer from one phase to the other takes place before the two phases are let to separate again.¹³ This separation process is reversible by contacting the solvent loaded with another immiscible phase that has a higher affinity for the solute than the organic phase.¹³ The transfer of solute from one phase into the solvent phase is referred to as extraction and the transfer of the solute from the solvent back to the aqueous phase is referred to as stripping.¹³ The organophosphorus extractants di-(2-ethylhexyl)phosphoric acid (D2EHPA) and (2-ethylhexyl)phosphonic acid mono-(2-ethylhexyl) ester (PC 88A) (EHEHPA) have been used for separation of REEs from leachates.^{6,15}

Aim of the study

Since the red mud may contain considerable amounts of critical raw materials, its use as secondary source should be investigated. We propose the development of a technology that does not only recover the economically interesting elements in red mud, yet also provides an option for the mitigation of alkalinity related risks after disposal. More specifically, this study focuses on the possibilities to recover REEs from Hungarian red mud with combined acid leaching and liquid-liquid extraction, lessening the inherent alkalinity [pH 11] of disposed red mud. In addition, we explore the possibility for heterotrophic bioleaching by benchmarking mineral acids versus small molecular weight organic chelators.

Materials and Methods

Three mineral acids were applied for the leaching (HCl, HNO₃, H₂SO₄). Experiments were conducted with C₆H₈O₇ and C₂H₂O₄, small molecular weight organic chelators. These can be biologically produced and were studied as green alternative to chemical leaching. After leaching, REEs were purified by liquid-liquid extraction using D2EHPA. To improve the recovery efficiency we investigated the leaching and extraction kinetics.

Origin of the Hungarian red mud

Briefly, during the Bayer process bauxite is digested with concentrated sodium hydroxide under elevated temperature and pressure to extract gibbsite (Al(OH)₃) and/or boehmite (γ-AlOOH).⁶ The separation of the NaAl(OH)₄-rich solution from the bauxite residue (red mud) usually occurs in settlers with flocculants⁶ and occasionally in pressure-decanters.^{6,16} Following the separation steps, the bauxite residues are washed in counter-current decantation washer.⁶ Finally the red mud is send to the disposal areas. The Hungarian alumina plant (Ajka, Hungary) uses 240 °C temperature and 29.6 atm pressure. After digestion, settling and washing, the red mud is pressure filtered to the disposal moisture content (20–30 wt%), then deposited in a dam at MAL Co. Ltd in Hungary.

Composition of the Hungarian red muds

Even after extraction in harsh conditions, red mud still contain valuable components from the original bauxite.¹⁷ Table 1 shows a summary of the amount of major and minor elements in red mud.

Table 1: Average composition of Hungarian red mud^{18,19,20}

Major elements	Concentration	Minor elements	Concentration	Minor elements	Concentration
Fe ₂ O ₃	41 %	Ga	89 ppm	Y	68 ppm
Al ₂ O ₃	17 %	V	730 ppm	Ni	31 ppm
SiO ₂	10 %	Zr	1230 ppm	Zn	20 ppm
TiO ₂	9 %	Sc	54 ppm	La	114 ppm
CaO	9 %	Cr	497 ppm	Ce	368 ppm
Na ₂ O	5 %	Mn	85 ppm	Nd	99 ppm

The red mud from Ajka (Hungary) is composed mainly of fine particles of silica, aluminium, iron, calcium and titanium oxides (Al₂O₃ 10–15 %; Fe₂O₃ 40–45 %; CaO 6–10 %; MgO 0.5–1 %; SiO₂ 10–15 %; Na₂O 5-6 %; TiO₂ 4–5 %) ²¹ along with economically interesting components (V ~ 1000 ppm; Ni ~ 250 ppm). In addition, critical raw materials were found to be present: Co (100 ~ ppm), Ce (< 400 ppm), La (~ 150 ppm), Nd (~ 130 ppm) and Pr (~ 100 ppm). ²²

Results and Discussion

The main objective was not only to maximise selective extractability of critical raw materials from red mud in terms of amounts, yet to achieve the highest "economic potential" of all elements in the respective leachates. The latter was calculated by the overall amount of element extracted × price of the respective element. It should be noted that the so calculated "economic potential" should not be seen in absolute terms, since they were based on pure element prices.

Leaching tests showed that La and Ce leaching efficiency was highest with HCl in comparison to HNO₃, H₂SO₄, C₂H₂O₄ or C₆H₈O₇. Interestingly, the REE leaching efficiencies using C₆H₈O₇ were comparable with those for mineral acids, however, requiring a higher process temperature above 90 °C (vs. 25 °C, resp.) using the same contact times. Comparing different HCl concentrations, the maximum metal leaching efficiency was achieved using 6 M HCl (for instance La ~ 98 % and Ce ~ 74 % the leaching efficiency, resp.). Dy was the most valuable metal using 6 M HCl, 60 °C, 24 h and S/L=100 g L⁻¹. Furthermore, REEs were purified by liquid-liquid extraction using D2EHPA. The selectivity could be controlled by varying the pH of the leachates, indicated by precipitation of Fe (Figure 2). Extraction yield of 96 % for Ce and 92 % for La from the leachate were achieved with D2EHPA extraction.

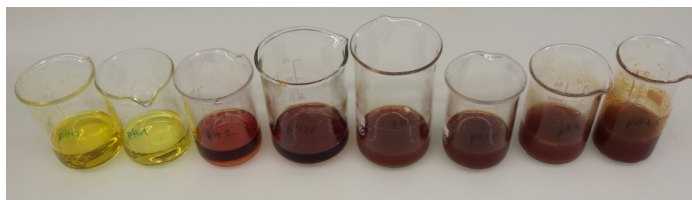


Figure 2: From left to right: higher applied pH, higher extractability indicated by the color of Fe in the leachate

Conclusions

This study presents a selective recovery method of REEs from red mud, the by-product of the aluminium production. Several parameters for instance leaching agents, contact time, temperature and solid to liquid ratio were investigated to optimise the leaching. Finally, the leaching process was carried out with 6 M HCl. Liquid-liquid extraction using D2EHPA was applied to purify REEs from the leachate and the achieved extraction efficiency percentages with D2EHPA were 96 % for Ce and 92 % for La. Although Hungarian red mud has low REEs concentration, methods developed can be transferred to others. $C_6H_8O_7$ can be used as green alternative, yet at expense of higher energy demand (T) or higher footprints (contact time). The economic potential should be rather used than relative extraction yields to ensure comparability of different studies.

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