

Geometallurgical investigation of Ion Adsorption Clays

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Abstract. We performed a mineralogical, geochemical and geo-hydrometallurgical study on Rare Earth Element (REE) enriched lateritic Ion Adsorption Clays (IAC). IAC are formed by hydrolysis-driven lateritic weathering of parental rocks under humid tropical conditions. These parental rocks contain significant amounts of REE-bearing minerals, which are liable to weathering. As a result of acidic soil conditions – indicated by a $\text{pH} < 4$ – aluminosilicates (mainly feldspar) are altered to kaolinite. RE^{3+} ions, released during the breakdown of REE minerals, migrate through the weathering system and are adsorbed onto the clay mineral surfaces. Parental rocks were identified as foid bearing diorites, syenites and highly REE enriched pegmatitic specimen by XRF, ICP-MS and QEMSCAN investigations. Lateritic Ion Adsorption Clay samples are mainly consisting of clay minerals, quartz and Fe-(hydr-) oxides and have an average REE concentration of ~500 ppm with a maximum of ~1200 ppm and a minimum of 150 ppm. On the basis of sequential extraction analyses, the Light Rare Earth Elements (LREE, Lanthanum - Europium) are preferentially adsorbed onto clay mineral and Fe (hydr-) oxide surfaces. The application of extraction methods showed a successful implementation of the non-Chinese IACs in hydrometallurgical process routes using mineral acids and/or salt solutions. The best leaching efficiencies could be achieved with sulfate based systems, particularly using a mixture of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$. The chosen leaching system affects the REE recovery whereas the leaching time increases the liberation of matrix elements.

Keywords. Rare Earth Elements, Ion Adsorption Clays, Parental Rocks, REE Minerals, QEMSCAN, Sequential Extraction, Hydrometallurgy

1 Introduction

Rare earth elements (REE) are used in a variety of high technology devices, for instance hybrid cars, smartphones and permanent magnets. They are typically and historically extracted from the conventional minerals monazite (REEPO_4) and bastnäsite ($\text{REECO}_3(\text{F}, \text{OH})$) which contain considerable amounts of radioactive elements and have only relatively low concentrations of the more valuable heavy rare earth elements (HREE, Gadolinium – Lutetium). These are currently almost exclusively supplied by the Ion Adsorption Clay (IAC) deposits of southern China (Chi and Tian 2008). This study presents a geo- and hydrometallurgical investigation of a potential Ion Adsorption Clay material and its parental rocks from outside China.

2 Geometallurgical Investigation of Ion Adsorption Clays and Parental Rocks

2.1 Geochemistry & Mineralogy

Based on geochemical analyses, the investigated parental rocks can be discriminated into SiO_2 undersaturated (foid-bearing diorite and syenite) and SiO_2 rich pegmatitic specimen. Whereas the former have a relatively low average REE concentration (~300 ppm), the latter are highly enriched in REE (average ~11000 ppm) and radioactive components Th (~1700 ppm) and U (~170 ppm). Additional valuable elements are Nb (~2600 ppm) and Zr (~10000 ppm). Both rock types show differing C1 normalization patterns (Fig. 1) after McDonough and Sun (1995). The pegmatitic rocks have distinctive negative Eu anomalies, whereas the other rock group shows no explicit anomaly at all.

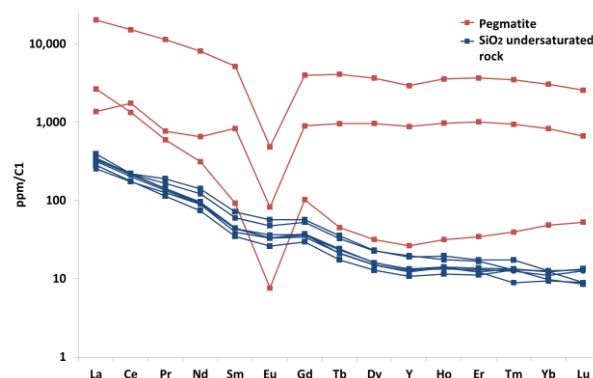
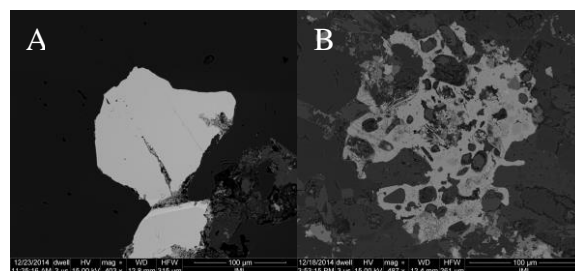


Figure 1. C1 normalized REE pattern

REE minerals are relatively abundant in pegmatitic rocks comprising of monazite (Ce, La), bastnaesite (Ce, La), pyrochlore, fergusonite (Y), zircon and thorite (Fig. 2, A-D). The majority of REE in SiO_2 undersaturated rocks is probably bound to zircon and apatite.



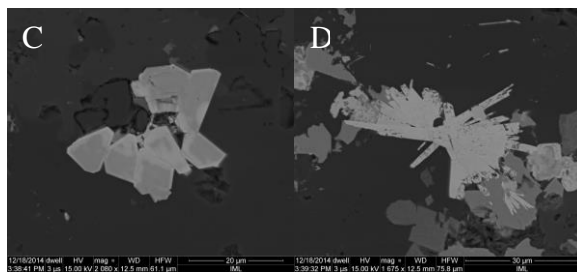
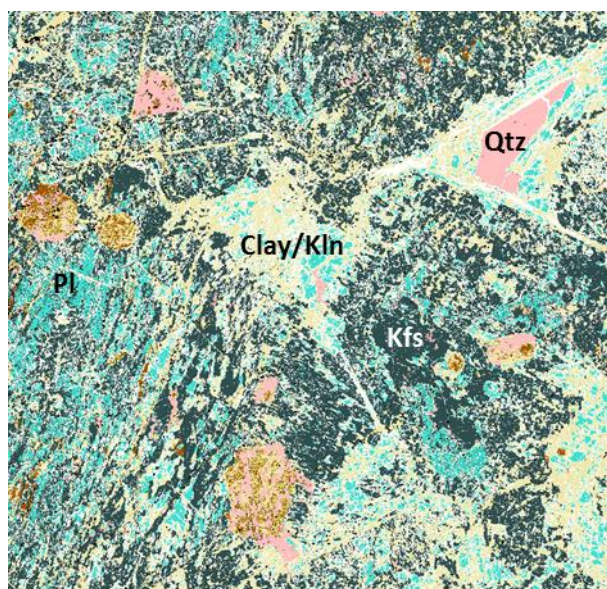


Figure 2. BSE images of Significant REE minerals in pegmatitic rocks; A monazite (Ce, La); B bastnaesite (Ce, La); C pyrochlore; D fergusonite (Y)

The primary minerals of the pegmatitic rocks are quartz (~40 vol. %), K-feldspar (~25 vol. %) and aegirine (20 vol. %), with minor amounts of plagioclase (~4 vol. %) and Fe-hydroxides (~4 vol. %). The SiO₂ undersaturated rocks mainly consist of plagioclase (~35 vol. %), K-feldspar and nepheline (~30 vol. %), Ca-amphibole (~25 vol. %) and augite (~5 vol. %).

During the weathering process aluminosilicates (mainly feldspar) are altered into clay minerals. The REE³⁺ ions are released by the breakdown of REE minerals and migrate through the weathering system whereby HREE are preferentially adsorbed onto clay mineral surfaces because of the increase in surface complexation constant related to the increasing atomic number within the REE series (Aagaard 1974).



2000 µm

Figure 3. QEMSCAN image of weathering reactions in parental rocks

The resulting lateritic Ion Adsorption Clay samples have an average REE concentration of ~500 ppm with a maximum of ~1200 ppm and a minimum of ~150 ppm, indicating a strong variability similar to the Chinese ores with concentrations between ~500 and ~3000 ppm (Foley et al. 2014). The Light vs. Heavy Rare Earth Elements (LREE vs. HREE) ratio is approximately 5:1. Weathering intensity calculations (chemical index of alteration; e.g. Nesbitt and Young 1982) demonstrate a constantly high value of ~90 % that is even higher than

the CIA range reported for Chinese IAC (~66-92 %; Wu et al. 1990, Murakami and Ishihara 2008). XRD analysis and Rietveld quantification revealed consequentially a high abundance of clay minerals with predominantly kaolinite (~22-80 wt.%), halloysite (~0-36 wt.%), nacrite (~0-11 wt.%) and dickite (~0-30 wt.%). Quartz contents (~4-40 wt.%) are highly variable depending on the sample origin. Minor proportions of zircon were identified (<1 wt.%; Fig. 4). Iron (hydr-) oxides occur in terms of goethite (~0-19 wt.%) and hematite (~0-3 wt.%). Minor amounts of gibbsite indicate a weak bauxitization (~0-7 wt.% with one exception of ~28 wt.%).

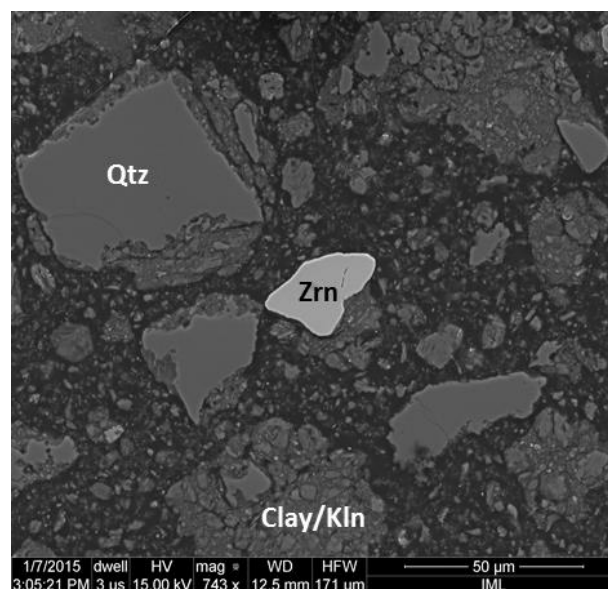


Figure 4. BSE image of the lateritic Ion Adsorption clay with the dominating minerals kaolinite and quartz in presence of zircon

Elemental change calculations after Nesbitt (1979), using Al₂O₃ as an immobile reference element (Murakami and Ishihara 2008), indicate a strong depletion of REE in laterites derived from pegmatites. In contrast, the laterites formed over SiO₂-undersaturated rocks are moderately REE enriched. This is because of the assumed relatively small volume of REE rich pegmatitic dykes within the alkaline complex that is involved in weathering and therefore provides less of its characteristics to the IAC. However, the proportion is significant as related to the ore body formation and REE enrichment.

2.2 Sequential Extraction & Hydrometallurgy

A sequential extraction using the method of Galan et al. (2003) was applied for the investigation of the bonding character of REE species in the lateritic samples. The process included four extraction stages suitable for the analysis of Fe-rich sediments (exchangeable fraction and carbonates, oxides, organic material and sulphides, residual fraction). Each fraction is obtained with a specific solvent leading to the extraction of individual components and their subsequent identification (Tessier et al. 1979).

The results show that the LREE are preferentially

adsorbed onto clay mineral and Fe (hydr-) oxide surfaces (fraction 1). La, Ce and Nd account for 68 % of the extracted REE proportion. Thereof 85% of La and Nd are present as exchangeable cations (1. fraction). Figure 5 presents the percentage distribution of all analyzed REE within the four fractions. With increasing atomic number, the REE become less incorporated in the exchangeable fraction and increasingly located in the residual fraction (4. fraction). 50 % of the total amount of Yb and Lu, respectively, is bound to matter that was dissolved within the last extraction stage and therefore present in the crystal structures of silicates (probably clay minerals and zircon). Only minor REE concentrations are available in fractions 2 and 3 (oxides, org. mat. and sulfides) with Ce as an exception, which is probably incorporated as Ce^{IV+} in Cerianite (CeO_2).

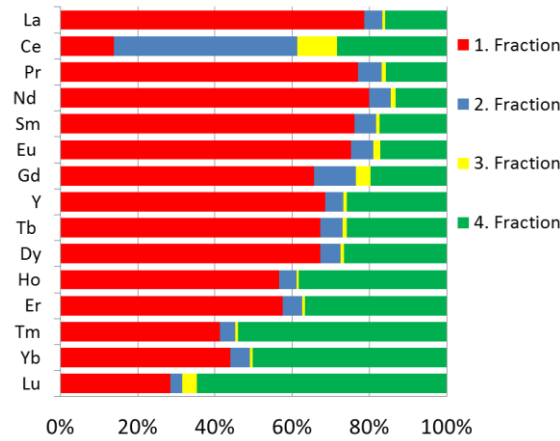
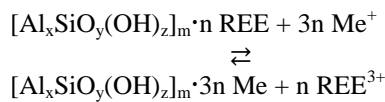


Figure 5. Results of the sequential extraction; distribution of specific REE in different fractions (1. Fraction: exchangeable cations; 2. Fraction: oxides; 3. Fraction: organic material and sulfides; 4. Fraction: silicates)

The industrial recovery of REE-bearing IACs is usually done by leaching the ore with electrolytic solutions of sodium- or ammonium-sulfates, -chlorides or -nitrates to liberate the adsorptive ligated REE. To keep the solute REE in solution an acidic pH is adjusted with mineral acids like HCl, HNO_3 or H_2SO_4 . High pH-values lead to less REE extraction yields because of hydrolysis. In comparison a decreasing pH increases the solubility of impurities like the matrix elements of IACs (e.g. Fe, Al and Si). The general leaching mechanism complies with an ion exchange of cations of the used electrolytic solutions, shown in formula 1, to liberate the adsorptive ligated REE (Zhang and Edwards 2013; Moldoveanu and Papangelakis 2013; Coppin et al. 2002).



Me \triangleq e.g. Na^+ or NH_4^+

1

according (Zhang and Edwards 2013):

x = 2, y = 5 and z = 4 (other ratios possible)

To verify the direct implementation of the studied IAC in state of the art process routes, leaching tests with mineral acids (HCl , HNO_3 , H_2SO_4) with different

concentrations (0.1 and 0.5 mol/L), pure salt solutions (Na^+ and NH_3^+ based, c = 0.5 mol/L) and composites are investigated. Constant parameters are the leaching time of 1 h at 30 °C with a solid:liquid-ratio of 1:5. After leaching, the suspension is filtrated. The metal concentration of the filtrate is analyzed with ICP-OES and the solids with XRF. Based on the elemental analysis, the REE extraction yield (R) and the selectivity (S) to major matrix elements serve as evaluation criteria.

The evaluation of sulfate, nitrate and chloride based leaching systems indicates an increased REE extraction yield of sulfate based systems. The experiments with single mineral acids as well as with single salt solutions point out the sulfate based reagents as the most favorable leaching system to extract REE from IACs. An increasing mineral acid concentration from 0.1 to 0.5 mol/L does not liberate a significant additional amount of REE but leads to a higher dissolution of impurities e.g. Fe and effects less selectivity as mentioned in the literature.

Sodium- and ammonium-sulfate-based reagents show similar leach results but a mixture of mineral acid (0.1 mol/L) and salt solution (0.5 mol/L) increases the REE metal yield by about 10 to 20 %.

As a result, the most efficient leaching system is presented in Figure 6. The graph is downscaled from sixteen to four selected REE with high contents in the initial material to minimize the effect of analytical errors (La, Ce, Nd representing the LREE and Y representing the HREE). The extraction yields indicate high REE recovery rates of 50 to 95 %. The decreasing recovery from La to Y is related to the sequential extraction results and confirms a decreasing adsorption behavior with increasing atomic number. It is supposed that fraction 1 (adsorbed REE) can be liberated at elevated process parameters. The anomaly of the reduced recovery rate of Ce can probably be explained with the +IV oxidation state which requires a more aggressive leaching environment for liberation. The kinetic evaluation of the extraction yields from 0 to 60 minutes indicates a direct liberation of REE with marginal increasing over time. This is a typical behavior of IACs because of the easy liberation of adsorptive ligated REE or oxides on the surface. To extract the remaining REE the crystal structure has to be destructed.

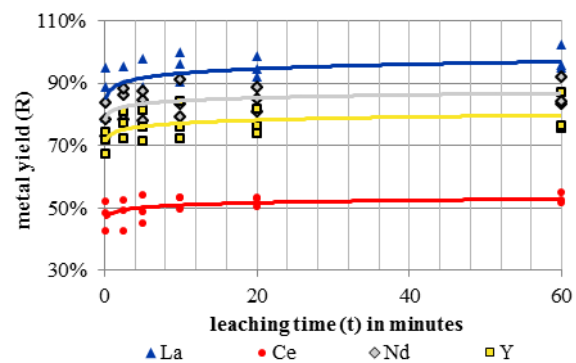


Figure 6. REE metal yield of direct leaching experiments (logarithmic approximation) (0.1 mol/L H_2SO_4 and 0.5 mol/L $(NH_4)_2SO_4$, 30 °C, solid:liquid-ratio 1:5)

This can be realized e.g. by time but leads to an

excessive liberation of matrix elements illustrated in Figure 7 which points out the quotient of the extraction yield of Nd to major matrix elements (Fe, Al, Ti, Si) depending on time (formula 2).

$$S(M_1:M_2) = R(M_1)/R(M_2)$$

$R(M_1)$: e.g. metal yield of Nd

2

$R(M_2)$: e.g. metal yield of Fe, Al, Ti or Si

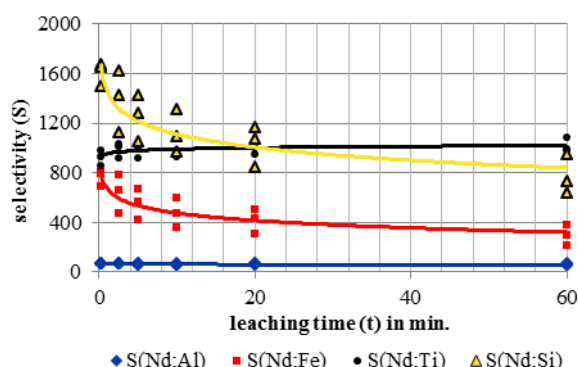


Figure 7. Selectivity of Neodymium and major matrix elements of direct leaching experiments (logarithmic approximation) (0.1 mol/L H_2SO_4 and 0.5 mol/L $(NH_4)_2SO_4$, 30 °C, solid:liquid-ratio 1:5)

3 Conclusion

Ion Adsorption Clays are formed under lateritic weathering in tropical to semi-tropical climates from parental rocks with high abundances of labile REE minerals. Investigated lateritic samples were derived from SiO_2 undersaturated and REE poor rocks as well as pegmatitic rocks with high REE concentrations due to the presence of REE minerals such as monazite (Ce, La), bastnaesite (Ce, La), pyrochlore and fergusonite (Y). During the breakdown of these minerals, RE^{3+} ions are released and attached onto clay mineral surfaces. The lateritic samples show a consistent mature weathering status and high abundances of clay minerals, mainly kaolinite and to a lesser content halloysite, nacrit and dickite. For laterites to form an Ion Adsorption Clay ore body it is a prerequisite to carry a high abundance of clay minerals and they must have been derived from a parent rock with a substantial REE-enrichment. The results of a sequential extraction analyses indicate that the majority of LREE are present in the exchangeable fraction, thus adsorbed onto clay mineral and Fe/Al (hydr-) oxide surfaces. With increasing atomic number REE are progressively located within the residual fraction (silicates).

Performed leaching experiments with the investigated IACs demonstrate possible high REE recovery rates with mineral acids and salt solutions. In comparison to chloride and nitrate based systems, the best leaching efficiencies could be achieved with sulfate based systems, particularly using a mixture of H_2SO_4 and $(NH_4)_2SO_4$. Short leaching times are favorable to prevent an excessive liberation of matrix elements especially Fe and Si.

Acknowledgements

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