

RECOVERY OF RARE EARTH ELEMENTS FROM CLAY MINERALS

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Abstract

Continuous development of advanced technologies has created increasing demand for rare earths elements (REE), with global emphasis on identifying new alternate sources to ensure adequate supply. Clay deposits containing physically adsorbed lanthanides are substantially lower grade than other types of REE mineral resources; however, their abundance in sub-tropical regions, existence as surface layers requiring low mining cost, and their high cation exchange capacity make them economically-important sources of rare earths. At the University of Toronto we have conducted a systematic study of clay minerals from various locations. It was found that REE are easily recovered via an ion-exchange mechanism during leaching with monovalent salt solutions under ambient conditions, based on a 3:1 stoichiometric ratio between the trivalent lanthanides and the exchange monovalent cation. The present paper reports on the most important findings of this investigation.

I. Background

Rare earths, also known as lanthanides, are a series of 17 elements with unique properties that make them essential for the hi-tech industry because of their various uses in high strength permanent magnets, lasers, automotive catalytic converters, fiber optics/superconductors, and electronic devices. They are grouped depending on the atomic number, in “light” rare earth elements (REE)—La, Ce, Pr, Nd, and “middle & heavy” REE—Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y. Because of the ongoing development of new advanced technologies, there is an ever-increasing demand for lanthanides in the international markets, with emphasis on identifying new resources to ensure adequate supply for present and future use. World production of REE is dominated by China, the United States and Australia; however, in terms of reserves and resources, China dominates the world potential with reserves estimated to be around 50% of the total while completely leading and controlling the global production at ~ 90%.¹ For the last 3 decades, R&D in the field of REE in most of the Western world has slowed down due to the import of these elements from China. Consequently, the development of specialized extraction, refining and processing technologies, including equipment and training of engineering expertise were allowed to lapse, creating thus a dependence on Chinese supplies. Starting with 2005 China – the undisputed leader in both REE innovation and trade, has been restricting yearly export quotas for REE ores in order to have enough resources for its own industries and to gain control over the global market, especially for the heavy and scarcer rare earths.² Consequently, the last decade has brought a renewed concerted global drive towards REE research and development, led by USA and Japan, with the dual scope of finding new resources and improving processing/extraction technologies, as summarized by Adachi, Imanaka and

Tamura.³

REE are part of many various rock-forming minerals, but the most commercially significant sources, as reviewed by Kanazawa and Kamitani,⁴ fall into the following categories:

1) Bastnasite, (REE, Ce)(CO₃)F, is a magma-derived fluorocarbonate mineral containing 65-75 %wt. light rare earth oxides (REO) and accounts for more than 80% of global REO production. The two major sources in the world for lanthanides are bastnasite deposits at Mountain Pass, California (U.S.A) – devoted solely to REE production, and Bayun-Obo, Inner Mongolia (China) – mined primarily for iron ore and REE as by-product.

2) Monazite, (REE)PO₄ is a light REE phosphate containing 55-65 %wt. REO, associated with granites and beach sands in Australia, Brazil and India. Until about 1965 monazite was the main REE source; since then, the use of monazite has been considerably reduced due to radioactivity caused by thorium and radium.

3) Xenotime (Y,REE)PO₄ is an yttrium-rich phosphate containing 25-60 %wt. Y₂O₃ and other heavy REE. It is mainly recovered as by-product of mining for titanium, zirconium and tin in Malaysia, Indonesia and Thailand.

4) Weathered Crust Elution-deposited Rare Earth Ores (common name: Ion-adsorption Clays) are aluminosilicate minerals (e.g. kaolinite, illite, and smectite) containing 0.05-0.3% %wt. REEs are physically adsorbed at sites of permanent negative charge. The ion-adsorption clay deposits are the result of in-situ lateritic weathering of rare-earth rich host rocks (granitic or igneous), which lead over geological times to the formation of aluminosilicate clays. These very fine mineral particles have the capability of adsorbing lanthanide ions released/dissolved during weathering. Sub-tropical climates present ideal conditions for this lateritic process to occur. The best example of this formation process exists in Southern China (latitudes 24-26°N), where many of such deposits are known to exist, as described by Bao and Zhao.⁵ In spite of their low grade, ion-adsorption clays account for ~ 35% of the China's total REE production, according to Yang et al.⁶

Carbonate and phosphate sources, in spite of being high grade, are associated with elevated recovery costs due to difficulty in mining, separation, beneficiation and need of aggressive conditions to dissolve the REE. For example, bastnasite is generally leached with concentrated H₂SO₄ or HCl, whereas monazite/xenotime concentrates need to be baked either in 98% H₂SO₄ or 70% NaOH to render REE soluble. Secondary REE sources include apatite and the so-called "hard-rock" deposits such as zircon, titanate, niobate, allanite, eudialyte, gadolinite, but these contain less than 30% REE and require even harsher conditions for breaking down the mineral matrix (e.g. caustic bake followed by acid leaching); the processing of these ores is mainly directed towards extraction of niobium, tantalum and zirconium.⁷

Although ion-adsorption clay deposits are substantially lower grade than other types of lanthanide sources, the lower grade is largely offset by the easier mining and processing, costs, and the very low content of radioactive elements (normally associated with yttrium). These deposits are mined by open-pit methods and no ore beneficiation is required. A simple leach using monovalent sulphate or chloride salt solutions at ambient temperature can produce a high-grade REO product.^{8,9,10} Because of their abundance in surface layers in

nature, ease of mining and processing, these clays warrant a detailed study as important sources of rare earths.

II. Formation of Weathered Crust Elution-deposited Rare Earth Ores (Ion-adsorption Clays)

The ion adsorption clay deposits of REE were first discovered in 1969 in the Jiangxi province (southern China) and declared a novel type of exogenous rare earth ore. Since then, more deposits were discovered and mined all throughout the South of China, as indicated by Figure 1.

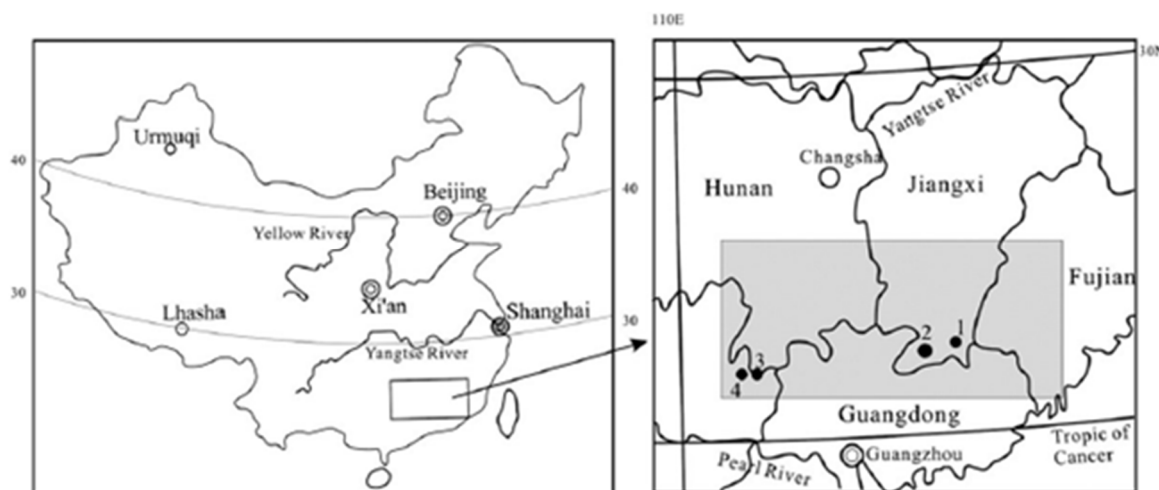


Figure 1: Locations of REE-bearing ion-adsorption clay ores in China⁵

The formation of this type of ore is due to physical, chemical and biological (microbial) weathering of REE-rich granitic and volcanic rocks under warm, humid, slightly acidic conditions in subtropical zones. According to Bao and Zhao,⁵ the weathering crusts are up to 30 m deep and divided into four layers: (A) An upper humic layer of quartz, organic matter and soil: 0–2 m thick, with very low/nil REE content; (B) a strongly weathered layer enriched in REE: 5–10 m thick with kaolinite, halloysite, quartz and mica; (C) a semi-weathered layer: 3–5m thick with kaolinite and sericite; (D) a weakly weathered bottom layer with the same mineral compositions as the host rock. 80-90% of the adsorbed REE report to the strongly weathered layer (B) whereas less than 15% are found in the semi-weathered later (C). Depending obviously on the nature of the original host rocks, the general components of the weathered ores are kaolinite, halloysite and mica, with a typical composition (as %wt.) of ~70% SiO₂, 15% Al₂O₃, 3-5% K₂O, 2-3% Fe₂O₃ and less than 0.5% of CaO, MgO and other elements.⁸ The metallogenic mechanism of formation for the weathered REE deposits, as proposed by Peng¹¹ and later expanded by Hendrick¹² is presented in Figure 2.

Considering the geological and climate conditions for the formation of REE-bearing weathered ores, there is no reason to limit the occurrence of this type of deposits within Chinese borders. While at the present time China is the only country to actively pursue and develop this type of resource to commercially produce REE, recent geological surveys (summarized by Chen¹³) have led to the discovery and investigation of similar ion adsorption clay deposits in South America¹⁴ and Africa,¹⁵ located in the same sub-tropical weathering areas as depicted in Figure 3.

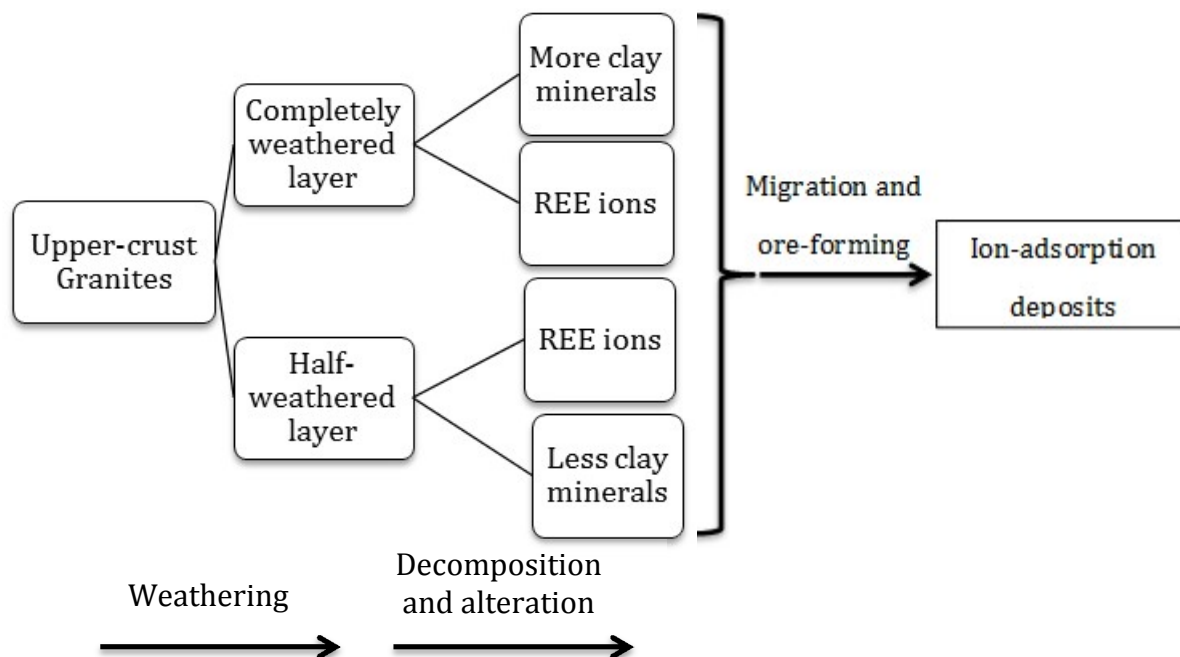


Figure 2: Metallogenic mechanism of formation for REE-rich adsorption-type ores (adapted from Peng¹¹ and Hendrick¹²)

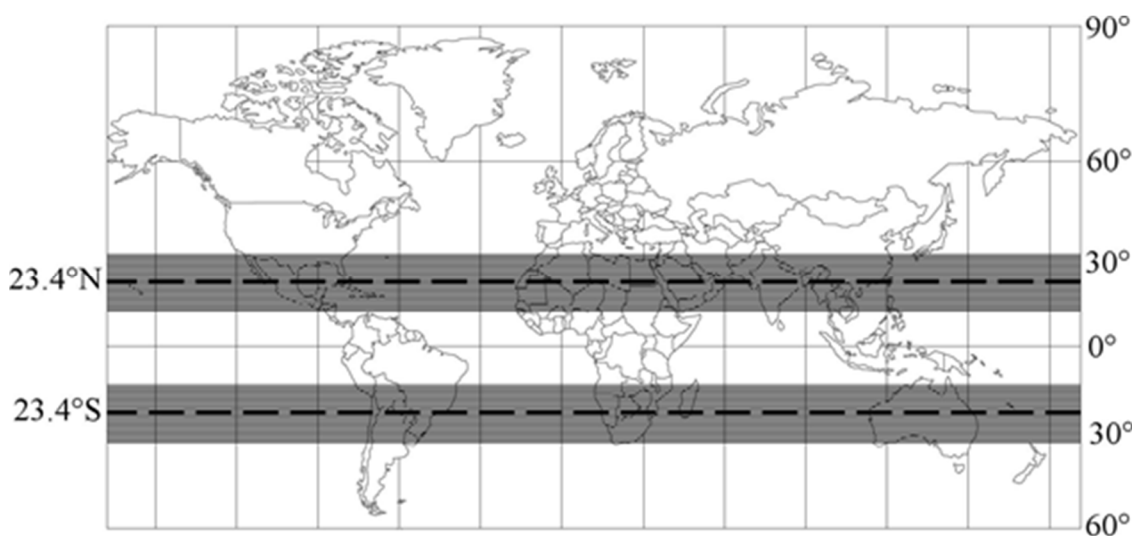


Figure 3: Area (shaded) favourable for ion adsorption clays formation

III. Nature of Rare Earth Elements in Ion-adsorption Clays

Clay minerals are part of the phyllosilicate class, containing layered structures of shared octahedral aluminum and tetrahedral silicon sheets; water molecules and hydrated cations can move in and out of the interlayer spaces. Very often, isomorphous substitution of one cation with another (of similar size but with lesser charge, e.g. Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+}) within crystal structures leads to a charge imbalance in silicate clays, which accounts for the

permanent negative charge on clay particles, thus the ability of clays to attract cations to the surface. Amphoteric -OH groups at the surface/edge of clays (i.e., silanol and aluminol) may also contribute to surface charge (pH-dependent reversible charge).¹⁶

According to Bradbury and Baeyens¹⁷ as well as Piasecki and Sverjensky,¹⁸ for acidic and near-neutral conditions (pH < 6.5-6.8), most of the surface-adsorbed lanthanides occur as simple or hydrated cations such as “clay-REE” or “clay-REE(H₂O)_n” species derived from straightforward cation-exchange reversible reactions at the permanent negative charge sites on the clays (physisorption); for pH > 7 the prevalent form is the hydrolyzed “clay-O-REE²⁺” species derived from permanent complexation reactions at the amphoteric surface hydroxyl groups (chemisorption) or soluble carbonate/bicarbonate complexes.⁸

Due to various weathering conditions (i.e. nature of host rocks, water and soil pH, temperature, pressure, redox conditions) there are three main categories of REE present in the ion-adsorption clays, as described by Chi and Tian⁸:

1. Colloid phase: REE deposited as insoluble oxides or hydroxides or as part of colloidal polymeric organometallic compounds. These species have low occurrence in ores at the slightly acidic natural conditions and can be recovered only by acid leach.
2. Exchangeable phase: REE occur as soluble free cations/hydrated cations or part of positively-charged complexes in solution adsorbed species on clays. These species account for 60-90% of total content of rare earths in ores and can be recovered by ion-exchange leaching with monovalent salts.
3. Mineral phase: REE part of solid fine particles with same mineral matrix as the host rocks (REE part of the crystal lattice). This phase usually accounts for the balance from the ion-exchangeable phase towards the TREE content and can be recovered only by aggressive conditions (alkaline bake and acid leach).

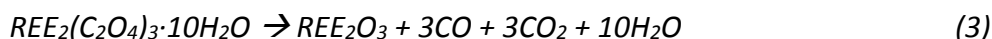
The vast majority of the ion-adsorption ores present the “negative cerium anomaly”, meaning that, contrary to the majority of lanthanide elements which are usually physically adsorbed as trivalent ions, Ce³⁺ can be easily oxidized by atmospheric oxygen (O₂) to Ce⁴⁺,¹⁹ and precipitates as cerianite, CeO₂. Consequently, the formation of the mineral cerianite facilitates a natural separation of Ce from the other adsorbed trivalent lanthanides, as described by Bao and Zhao,⁵ and makes it impossible to be recovered by ion-exchange leaching.

Depending on the nature of the original host rocks, other metals will get dissolved and carried downstream during the weathering, decomposition and alteration processes. The main impurities associated with the ion-adsorption ores are usually Al, Mg, Ca, Mn, Zn and Fe. While most base metals occur as part of the mixed mineral phase and do not leach out during the mild ion-exchange REE leaching conditions, Al especially and to a lesser extent Ca and Mg constitute the major impurities physically adsorbed on clays that are liable to get desorbed during the process along with the lanthanides.^{8,14}

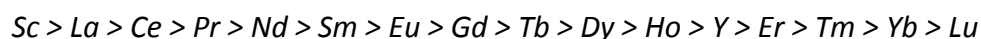
IV. Overview of Leaching Technologies for the Ion-Adsorption Clays

As previously described, the ion-adsorption clays contain anywhere between 0.05 to 0.3 wt.% rare earths, out of which 60-90% occur as physically adsorbed species recoverable by simple

ion-exchange leaching. In the typical procedure, the ores are leached with concentrated inorganic salt solutions of monovalent cations. During leaching, the physisorbed REE are relatively easily and selectively desorbed and substituted on the substrate by the monovalent ions and transfer into solution as soluble sulphates or chlorides, following a 3:1 stoichiometry (Eqn. 1). Solubilized REE are usually selectively precipitated with oxalic acid to form oxalates (Eqn. 2) that are subsequently converted to REO via roasting at 900 °C according to Eqn. 3. Finally, the mixed REO are separated into individual REE by dissolution in HCl and fractional solvent extraction.



Various research conducted on the desorption of REE from clays via ion-exchange leaching^{8,9,10} indicated that, regardless of the initial content, not all REE reached similar extraction levels. Coppin et al.²⁰ reported that the amount of trivalent lanthanide ions adsorbed on smectite and kaolinite was inversely proportional to the ionic radii and pointed to a fractionation during selective sorption of lanthanides, with heavy elements (i.e., higher atomic number: Tb to Lu) being adsorbed stronger than the light ones (i.e., La to Gd). They related this behavior to the “lanthanide contraction” in the ionic radii going from light to heavy REE. Based on these observations, it was inferred that desorption must exhibit a similar trend, with heavy REE being more difficult to extract, probably according to the trend



Ever since the discovery of the weathered crust elution-deposited rare earth ores in the Jingxi province about 45 years ago, China was at the forefront of research and development of this kind of unique deposits, applying the ion-exchange leaching procedure for the extraction of lanthanides via three successive generations of technology, as summarized by Chi and al.²¹ and presented below.

The first generation leaching technology –batch leaching with NaCl

In the early 1970s, the ores were processed by opencast mining, sieved and leached with ~1M NaCl in barrels, followed by oxalic acid precipitation. The main disadvantages of this initial approach were small scale, low yields, high lixiviant concentration needed and poor product quality (<70% TREO content due to Na oxalate coprecipitation), which greatly surpassed the advantages of extremely low costs and fast processing times. By mid-1970s the procedure was changed to bath leaching in concrete pools in order to increase production; however, the main disadvantage of low product purity remained and, because of the largely unregulated and illegal/clandestine mining and extraction practices, the environmental impact was devastating, including severe loss of vegetation and biodiversity, soil erosion and water contamination (both streams and phreatic).

The second-generation leaching technology – batch and heap leaching with (NH₄)₂SO₄

In the early 1980s, 1M NaCl was replaced by ~ 0.3M (NH₄)₂SO₄ as lixiviant for batch leaching, which required less reagent consumption due to increased desorption capabilities of NH₄⁺ as

compared to Na^+ and led to improved final product purity ($> 92\%$ TREO content). The procedure was so successful that it became the primary leaching method for the next approximately 20 years and largely contributed to the intense development of REE ion-adsorption research. However, the second-generation batch leaching technology led to environmental impact as well, due to mining-related deforestation and discharge of tailings and was ultimately replaced in early 1990s by the heap leaching procedure.

In the traditional heap leaching procedure, the soil pile (1.5-5 m high) is built on a flat impermeable (leak-proof) layer 5-20 cm thick inside a cofferdam ~ 50 cm high as to prevent solution overflow. The lixiviant is injected into the top of the pile at a solid to liquid (S:L) ratio of $\sim 0.25:1$ and accumulates at the bottom in the collecting ditch. Washing is performed with clean water at a S:L ratio of $\sim 0.6:1$; depending on the size of the ore heap, leaching time ranges from 100 to 320 hours and REE extraction can reach up to 90%. This procedure is very well suited for the processing of very low-grade ores.

The third-generation leaching technology – in-situ leaching with $(\text{NH}_4)_2\text{SO}_4$

The intense and largely unregulated use of successful batch and heap leaching with ammonium sulphate for ~ 2 decades led to severe and long-lasting environmental, ecological and health damages in southern China; as an example based on Yang's paper,⁶ by 2010 the REE mining in Guangdong region alone has left ~ 302 abandoned mines, 191 million tons tailings and 153 km^2 of destroyed forests.

In June 2011, in an effort to regulate the industry and deal with the environmental effects, the Chinese government enforced a ban on surface mining and batch/heap leaching while implementing mandatory in-situ leaching technology for the processing of the ion-adsorption clays, as being more advantageous in terms of surface vegetation clearing and soil disturbance. The basic principle of in-situ leaching (also called "solution mining") is injection of leaching solution directly into the natural orebody and retrieval of the pregnant solutions for further processing. Leaching holes with a depth of 1.5-3 m and diameter of ~ 0.8 m are drilled 2-3 m apart, for up to 100 m, the lixiviant ($\sim 0.3 \text{ M } (\text{NH}_4)_2\text{SO}_4$) is injected at high pressure, flows through the pores of the orebody and the loaded leach solution is pumped above-ground through the recovery wells; the whole process (including injection of water for washing) can take up to 400 days and ultimately 85-90% of REE are extracted.

The in-situ leaching technique is also currently applied in China for the recovery of residual REE from the tailings of older batch and heap leaching operations.

The implementation of in-situ leaching requires comprehensive geological surveys - specific to each site - in order to determine the hydrogeological structure of the area, ore characteristics, grade, orientation and the surrounding rock infiltration properties. The procedure can only be applied to an orebody with suitable permeability and placed over solid bedrock without fissures. Failure to conduct diligent geological surveys may result in serious environmental degradation such as underground water contamination, mine collapse, landslides and severe loss of REE recovery.

V. Evaluation of Leaching Potential of Various Ion-adsorption Clays at University of Toronto

As new ion-adsorption REE deposits are being explored and discovered in the rest of the world, research on REE extraction from clays has expanded outside of China as well. For the last five years, the University of Toronto has conducted systematic in-depth studies on the leaching chemistry and optimum conditions for REE extraction from clay samples obtained from various geographical locations. Overall, it was determined that, under atmospheric conditions, the leaching power of monovalent ions for REE extraction depends on the hydration energy of the exchange ion, following the order $\text{Cs}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Li}^+$, in both sulphate and chloride.⁹ Batch leaching studies also revealed that the ion exchange process achieved equilibrium in as little as 5 minutes, regardless of the experimental conditions; ambient temperatures and moderately acidic pH values (4-5) represent optimum conditions for maximum REE recovery.¹⁰

Based on those previous studies, a benchmark leaching procedure was established and research has been conducted at the University of Toronto in order to compare leaching characteristics among different clay samples obtained from Africa, Asia and South America and evaluate lanthanide extraction. The final aim is to develop a fully contained optimized process for field implementation that minimizes the impact to environment by providing options for efficient reagent use, maximized extraction and recycle/regeneration of the lixiviant.²²

Experimental

Solid Characterization

The REE contents of the clay samples were determined by acid digestion at 220°C, using the Ethos EZ microwave digestion system, followed by inductively coupled plasma optical emission spectrometry of the solution (Agilent 720 ICP-OES).

Batch Leaching Tests

The leach solutions were prepared using ACS reagent grade ammonium sulphate and deionized water. The benchmarked procedure for leaching is: 0.5M $(\text{NH}_4)_2\text{SO}_4$ (natural pH ~ 5.2), ambient conditions, liquid to solid (L:S) ratio of 2:1 (vol./mass), 30 minutes total time. The slurry was agitated via magnetic stirring then the mother liquor was separated by vacuum filtration. The filter cake was washed by deionized water, and the wash water was collected separately for analysis. The resultant solutions were diluted with 5% (vol.) nitric acid and analysed by ICP-OES to calculate the REE extractions.

Results and Discussion

Table 1 shows the REE content (as %wt.) of the various clay samples tested while Table 2 shows the relative distribution of individual REE in the clays.

Table 1: REE content of ion-adsorption clays from different geographical origins

Origin	Africa					Asia		South America
REE (wt%)	A1	A2	A3	A4	A5	B1	B2	C1
Y	0.029	0.014	0.018	0.012	0.010	0.157	0.047	0.120
La	0.175	0.029	0.179	0.046	0.025	0.007	0.098	0.045
Ce	0.026	0.017	0.022	0.045	0.028	0.006	0.020	0.012
Pr	0.028	0.007	0.027	0.012	0.004	0.003	0.019	0.010
Nd	0.100	0.023	0.088	0.026	0.016	0.012	0.069	0.029
Sm	0.017	0.004	0.017	0.006	0.004	0.004	0.018	0.006
Eu	0.001	0.001	0.001	1.76E-04	4.76E-04	6.36E-05	0.001	0.002
Gd	0.011	0.004	0.009	0.003	0.003	0.015	0.013	0.010
Tb	0.002	0.001	0.001	0.001	1.06E-04	0.004	0.002	0.006
Dy	0.006	0.002	0.002	0.002	0.001	0.026	0.010	0.022
Ho	0.001	0.001	4.60E-04	3.33E-04	1.43E-04	0.005	0.002	0.007
Er	0.002	0.001	0.015	0.012	0.001	0.038	0.025	0.021
Tm	2.00E-04	8.69E-05	6.85E-05	2.32E-06	0.001	0.004	0.002	0.005
Yb	0.002	0.001	0.001	0.001	0.000	0.016	0.003	0.026
Lu	2.66E-04	2.66E-04	2.53E-04	1.71E-04	2.40E-04	0.002	4.95E-04	0.005
TREE	0.399	0.108	0.380	0.165	0.095	0.300	0.330	0.326

Despite total rare earth element (TREE) content being consistent with grades expected for the ion-adsorption clays, no specific pattern of preferential REE accumulation and distribution was observed, except that all ores seem to be rich in La and Y and Nd; although some similarities in terms of relative composition are observed within clays originating from the same geographical areas (e.g. A1 through A5), there is no consistent trend. This is probably due to wide variations in composition of original host rocks and incongruent dissolution-adsorption processes during the weathering processes.

The clay samples listed in Table 1 were leached using the benchmarked procedure described above to investigate the terminal REE extraction levels (shown in Table 3) and TREE leaching kinetics, respectively (presented in Figure 4).

From data in Table 3 it can be observed that all the minerals investigated are the ion-adsorption type, i.e., the lanthanides are physically adsorbed and can be easily recovered via a simple ion-exchange leaching procedure, as described by Moldoveanu and Papangelakis.^{9,10} The extraction levels vary between 40 to 80%, consistent with the predicted exchangeable REE percentage, as described by Chi and Tian⁸. Again, there is no consistent trend regarding REE desorption within clays of similar geographical origin; this could be explained in terms of:

The ores contain various mixtures of clay materials with different cation-adsorption capacities, i.e., clays with lower cation exchange capacity (CEC) such as kaolinite will adsorb less ions than the ones with larger CEC such as smectites, hence less is available for desorption (possible observed for clays A4 and A5).

Table 2: Relative distribution of REE within clay samples

Origin	Africa					Asia		South America
REE (%REE)	A1	A2	A3	A4	A5	B1	B2	C1
Y	7.2	12.9	4.6	7.0	10.7	52.5	14.4	36.9
La	43.8	26.8	47.0	27.6	26.7	2.2	29.7	14.0
Ce	6.4	16.1	5.7	27.4	30.0	2.1	6.0	3.6
Pr	7.0	6.1	7.2	7.4	4.2	0.9	5.8	3.0
Nd	24.9	21.6	23.2	15.5	16.7	3.9	20.8	8.9
Sm	4.4	4.1	4.4	3.4	3.7	1.3	5.6	1.8
Eu	0.2	0.8	0.2	0.1	0.5	0.0	0.3	0.7
Gd	2.8	3.9	2.4	2.1	2.9	5.2	4.0	3.0
Tb	0.4	0.6	0.3	0.3	0.1	1.3	0.6	1.7
Dy	1.4	2.1	0.6	1.4	1.5	8.7	3.0	6.9
Ho	0.2	0.7	0.1	0.2	0.2	1.8	0.6	2.0
Er	0.6	1.2	4.0	7.0	1.4	12.8	7.6	6.4
Tm	0.1	0.1	0.0	0.0	0.6	1.2	0.5	1.5
Yb	0.4	1.0	0.2	0.5	0.4	5.3	1.0	8.0
Lu	0.1	0.2	0.1	0.1	0.3	0.7	0.1	1.6
TREE	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 3. Final REE extraction from ion-adsorption clays from different geographical origins

Origin	Africa					Asia		South America
%E	A1	A2	A3	A4	A5	B1	B2	C1
Y	77.3	72.6	77.5	67.1	57.2	80.5	79.9	70.8
La	83.6	76.9	73.3	66.4	61.2	85.0	80.5	82.9
Ce	0.0	16.9	12.7	6.8	11.6	0.0	0.0	35.6
Pr	75.1	65.0	84.7	74.1	35.1	62.9	69.4	72.8
Nd	80.8	74.1	83.7	68.0	46.0	86.3	87.9	83.2
Sm	90.6	85.2	86.8	66.3	96.4	43.1	81.2	76.9
Eu	62.1	79.0	62.0	43.8	84.3	61.3	83.0	36.2
Gd	82.6	63.0	79.8	74.8	62.3	90.1	84.9	61.6
Tb	84.1	62.8	23.7	19.2	37.3	91.5	90.1	35.6
Dy	80.9	76.3	90.4	74.2	52.2	87.5	79.7	61.5
Ho	75.5	0.0	97.7	96.9	97.5	82.9	77.2	51.8
Er	86.8	73.5	80.9	63.0	44.7	75.2	91.5	53.0
Tm	53.4	79.4	11.2	23.1	7.0	57.9	26.8	47.0
Yb	73.2	64.0	9.4	16.0	25.4	77.9	73.2	61.9
Lu	52.3	34.9	18.9	31.7	12.2	78.5	67.5	51.5
TREE	76.6	64.0	72.8	58.9	42.6	80.3	82.1	68.7

The overall exchangeable fraction of REE is low, regardless of the high REE content, the balance being the matrix-bound lanthanides (possibly observed for clays C1).

As a general common trend for all clays, cerium does not exhibit large extraction due to its presence mostly as CeO_2 while some of the heavy REE also show poor extraction probably because of the stronger adsorption, as described by Coppin et al.²⁰

In terms of extraction kinetics, all materials investigated showed a common trend of fast REE desorption which is the typical behaviour of the ion-adsorption minerals. While each clay sample possesses a slightly different REE content and REE extraction end point, it can be seen that extractions reach the terminal levels in a very similar fashion, typically reaching plateau in less than 15 minutes of batch leaching time. The authors demonstrated¹⁰ that desorption kinetics are very fast independently of leaching conditions such as temperature, pH, and agitation, which influence only terminal extraction levels.

Conclusions

Past and ongoing research conducted at University of Toronto demonstrated the existence and commercial potential of ion-adsorption clay deposits outside China and established a unified benchmark procedure for REE leaching from these types of minerals. It was found that, in spite of variations in clay origin and REE content, all REE consistently reached peak extraction levels under ambient conditions with fast kinetics. However, the terminal extractions were generally clay and element-specific.

Based on those studies, an optimized process ready for field implementation is currently being developed, that highly minimizes the impact to environment by providing options for efficient reagent use, maximized extraction and recycle/regeneration of the lixiviant.

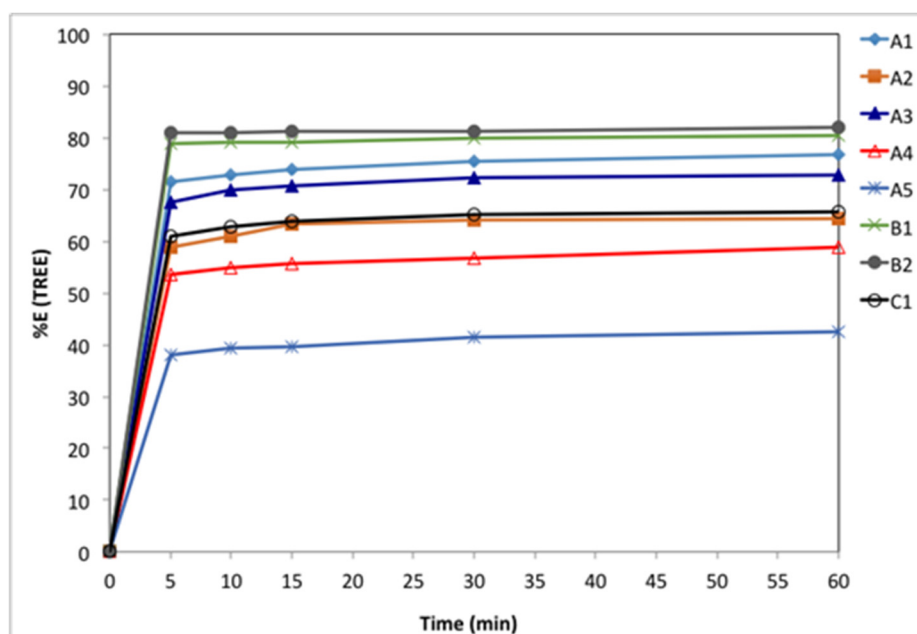


Figure 4: Kinetic response of ion-adsorption clays from various geographical origins to benchmark leaching conditions (0.5M $(\text{NH}_4)_2\text{SO}_4$, 60 min leaching under ambient conditions)

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