



# Effects of thermal pre-treatment and ore dryness on the recovery of lanthanides from ion-adsorption clays



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## ABSTRACT

The present research evaluated lanthanide desorption levels from ion-adsorption clays subjected to thermal pre-treatment at various temperatures in the range 100–900 °C. The authors identified macro- and micro-structural changes occurring in the clays during heating and related the observed trends to the water content and rare earth elements (REE) desorption behavior during subsequent ion exchange leaching, in order to gain a better understanding of how temperature and moisture may affect the overall REE recovery, hence impacting the ore processing route.

It was found that the total lanthanide extraction from clays pre-heated in the range 100–300 °C increased with the temperature, then decreased drastically, reaching near-zero levels for the range 700–900 °C. This trend was explained in terms of improved clay permeability achieved upon elimination of pore and adsorbed water molecules in the interval 100–300 °C, which facilitated better lixiviant access to the REE adsorption sites. The subsequent decrease in REE extraction in the interval 300–900 °C was related to the loss of hydroxyl groups from the aluminosilicate matrix (dehydroxylation), resulting in irreversible REE fixation to the surface and major structural changes such as layer collapse, loss of crystal structure and vitrification, with the ultimate result of completely blocking lixiviant access to the adsorbed cations.

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## 1. Introduction

Rare earth elements (REE) are a collection of sixteen chemical elements, namely scandium, yttrium, and fourteen of the fifteen naturally-occurring lanthanides (excluding promethium); the former two are included as they occur with the latter in the same ore deposits and have similar properties. Their unique properties make them essential for the hi-tech industry, with applications in permanent magnets, lasers, automotive catalytic converters, fiber optics, superconductors, alloys, and catalysts (Gupta and Krishnamurti, 2005).

China dominates the global REE potential with deposits comprising ~50% of the total reserves, while also leading and controlling the world production at ~90% (USGS, 2011). Starting with 2005, China has been restricting yearly export quotas for REE concentrates, in order to have enough resources for its own industries and exercise control over the global market (Hurst, 2010). Consequently, the last decade has brought a renewed global drive towards REE research and development, with the dual scope of identifying new resources to ensure adequate supply, and improving processing and extraction technologies, as summarized by Adachi et al. (2010).

Over 90% of the world's economically recoverable rare earth elements are found in rich primary mineral deposits such as bastnaesite (carbonate-based ores containing up to 70% REE), and monazite/xenotime (phosphate-based ores containing 55–60% REE). In spite of being high grade, these sources are associated with elevated recovery costs due to difficulties in mining, beneficiation, and the need for aggressive conditions to liberate the REE (Gupta and Krishnamurti, 2005); additionally, these ores are usually associated with highly-regulated radioactive elements (U and Th), leading to processing concerns and waste disposal issues.

One of the major commercially viable secondary sources of rare earths are the weathered crust elution-deposited rare earth ores (also known as “ion-adsorption clays” or “ionic clays”), containing 0.05–0.5% w/w rare earth oxides (REO) adsorbed on the surface of mixed clay minerals. The formation of this type of ore is due to physical, chemical and microbial weathering of REE-rich granitic and volcanic rocks under warm, humid, slightly acidic conditions in subtropical zones. Presently, China is the only country to pursue this type of resource for commercial REE production, these deposits accounting for 35% of Chinese REO output since 2009 (Yang et al., 2013). However, recent geological surveys have led to the discovery and investigation of similar deposits in South America (Rocha et al., 2013) and Africa (TRE Project, 2013). 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 (shallow deposits), and

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the low content of radioactive elements normally associated with the heavy REE in bastnasite.

Under acidic and near-neutral conditions, most of the adsorbed lanthanides (60–90% of the total REE content) occur as free or hydrated cation species electrostatically bound on the surface at sites of permanent negative charge via a pH-independent reversible physisorption; for  $\text{pH} > 7$ , the main REE surface species are permanently chemisorbed complexes (Bradbury and Baeyens, 2002; Piasecky and Sverjensky, 2008; Chi and Tian, 2008). A simple ion-exchange leach using monovalent sulfate or chloride salt solutions at ambient temperature can produce a high-grade REO product, as described by Chi and Tian (2008) and more recently Moldoveanu and Papangelakis (2012, 2013). During the process, the physisorbed REE are relatively easily desorbed and transferred into solution as soluble sulfates or chlorides, being replaced by the exchange monovalent cation, following a theoretical 3:1 stoichiometry (Eq. (1)).



Modern technologies implemented for the economical processing of low-grade ores such as the ion-adsorption clays are heap and in-situ leaching, as described by Chi et al., 2013. In the traditional heap leaching procedure, the ore is stacked in “heaps” while the lixiviant is injected into the top of the pile and the loaded solution is collected at the bottom, whereas the basic principle of in-situ leaching (also called “solution mining”) is injection of leaching solution directly into the natural orebody and recovery of the pregnant solutions for further processing. The ores subjected to these two processes have widely different initial moisture content. While the underground clay deposits can have a moisture content up to 20%, based on the natural tendency of clays to retain water and swell (Meunier, 2005), the heaps are often kept for extended periods of time under direct sun and wind (considering the subtropical location of these deposits), undergoing thus a heating and drying process before being subjected to leaching. Although the effects of temperature on the physical, mechanical and cation retention properties of clays have been widely reported, there is no known study at the present that investigates the effect of heat pre-treatment and moisture content on the REE recovery from ion-adsorption clays.

It is also well documented that thermal treatment irreversibly alters the physical and mechanical properties of clays: heat impacts on strength, plasticity, permeability, particle size, specific gravity, etc. (Laloui and Cekerevac, 2003; Tan et al., 2004). Additionally, it has been demonstrated that thermal treatment of clays influences the cation exchange capacity (CEC) (Sarikaya et al., 2000; Ouhadi et al., 2010), surface acidity (Noyan et al., 2006) and zeta potential (Ramachandran and Somasundaran, 1986). However, most of these studies were concerned predominantly with changes in various clay properties upon heating and rehydration, and not reporting on the leaching behavior of surface adsorbed species. Consequently, several testing protocols that intend to evaluate REE leachability from ionic clays, often performed in laboratory settings outside the mining area, include a heat pre-treatment (or calcination) step for pre-shipment sterilization reasons, and are liable to produce results differing from an actual process in which “as is” material would be processed.

The aim of the present research is to evaluate and compare lanthanide desorption levels from ion-adsorption clays previously subjected to thermal treatment at various temperatures. For this purpose, we investigated the macro- and micro-structural changes occurring in clays during heating and relate the observed trends to the water content and lanthanide desorption behavior during ion exchange leaching, in order to gain a better understanding of how temperature may affect the overall REE recovery, hence impacting the ore processing route.

## 2. Experimental

### 2.1. Materials and analytical procedures

For the preparation of all solutions used in the present work, de-ionized water and ACS-grade reagents were used. Two types of natural clays of African origin and known to contain adsorbed REE were tested, referred to C1 (Clay 1) and C2 (Clay 2), respectively. X-ray Fluorescence (XRF, Bruker AXS S2 Ranger) was employed to determine the overall bulk chemical composition of clays. The REE content was determined by acid digestion at 220 °C (Ethos EZ microwave system) followed by Inductively-Coupled Plasma optical emission spectrometry on the solution (ICP-OES, Agilent 720). X-Ray Diffraction (XRD, Phillips PW3719) and Thermo-Gravimetric Analysis (TGA, STD Q600) were used to gain additional information about the nature and behavior of the solids. The composition of all liquid phases following leaching was analyzed by ICP-OES.

### 2.2. Experimental procedure

#### 2.2.1. Thermal treatment

100 g of each of the clay samples were maintained at the selected temperature for 3 h (previously determined to be sufficient for reaching equilibrium in terms of mass loss); a vacuum oven (Isotemp®, Fisher Scientific) was used for 100 and 200 °C, while a muffle furnace was employed for higher temperatures (300, 500, 700 and 900 °C, respectively). Immediately following heat treatment and slight cooling (to allow safe handling), the clays were packaged in plastic bags and stored in the desiccator, to avoid additional moisture uptake prior to leaching.

#### 2.2.2. Batch leaching tests

The procedure involved 50 g clays, 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  (natural  $\text{pH} \sim 5.2$ ), ambient conditions, liquid to solid (L:S) ratio of 2:1 (vol./mass), moderate stirring to ensure slurry suspension, and 30 min total time. Based on previous work, desorption kinetics are very fast (<15 min) and independent of leaching conditions such as temperature, pH, and agitation, which influence only terminal extraction levels (Moldoveanu and Papangelakis, 2013). At the end of the experiment, the mother liquor was separated by vacuum filtration. The filter cake was washed twice with deionized water of adjusted pH 5 (L:S = 2:1), dried in the oven at 50 °C (overnight), weighed and stored, while the mother liquor and wash water collected after filtration were diluted with 5% (v/v)  $\text{HNO}_3$  and analyzed for REE content.

#### 2.2.3. Clay water saturation (soaking)

In order to assess the influence of water saturation of clays on REE extraction, and therefore to evaluate an in-situ leaching scenario, 50 g samples of original and pre-heated C1 (at 200 °C for 3 h) were soaked in de-ionized water for one week, vacuum filtered, air dried in the fume hood under ambient conditions for 24 h and leached following the procedure described in Section 2.2.2.

## 3. Results and discussion

### 3.1. Clay composition

The bulk chemical composition of clays (Table 1), determined by XRF, is similar for both materials and characteristic of the typical weathered ores containing mixed aluminosilicates, mainly kaolinite/halloysite ( $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ ), quartz ( $\text{SiO}_2$ ) and mica ( $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ ); as described by Peng, 1991 and Chi et al., 2013, these minerals are rich in Si, Al, Fe and K. The total REE (TREE) content, determined by ICP-OES, is 0.4% (w/w) for C1 and 0.18% (w/w) for C2, respectively. The XRD spectra of the two “as is” samples indicated that C1 has a slightly higher content of mica, which could explain the higher TREE content of C1 (due

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