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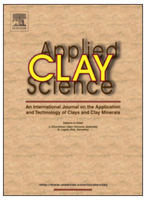

Research paper

Quantification and comparison of the reaction properties of FEBEX and MX-80 clays with saponite: Europium immobilisers under subcritical conditions

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ABSTRACT

The evaluation of the retention mechanisms in FEBEX and MX-80 bentonites, selected as reference materials to construct engineered barriers, carries major implications in the safe storage of immobilisation capacity through a recently discovered chemical retention mechanism and the structural analysis of the reaction products. Hydrothermal treatments were accomplished with immobilisation capacity through a recently discovered chemical retention mechanism and the structural analysis of the reaction products. Hydrothermal treatments were accomplished with $Eu(NO_3)_3$ (^{151}Eu and ^{153}Eu, with 52.2% ^{153}Eu) and spiked with radioactive ^{152}Eu for the quantification of the reactions. Results were compared with saponite as the reference smectite. The strong dependence of the reaction parameters with temperature and time was quantified and the reaction velocity was evaluated. The velocity follows these trends: 240 days are needed for the total retention of europium for temperatures over 200 °C; below 150 °C, significantly longer reaction times, on the order of three years, are required to complete the reaction. Clays do not influence velocity rates, but the retention capacity of bentonites remains lower than for saponite. At 300 °C, the milliequivalents retained by the three clays are consistently over CEC. The structural analyses reveal not only adsorption of europium but also the presence of $Eu(OH)_3$ precipitation and Eu_2SiO_3 confirming the existence of a chemical reaction.

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1. Introduction

In many countries, the development of Deep Geological Repositories (DGR), for the storage of high-level radioactive waste (HLRW) is based on a system of multiple barriers. Most safety within the repositories relies on the engineered barrier (Savage and Chapman, 1982). Clays present low permeability, and high sorption and swelling capacity, which makes them ideal materials for natural and engineered barriers for nuclear waste isolation (Pusch, 2006). A clay barrier is able to delay the diffusion and immobilise, in certain experimental conditions, the radioactive wastes through a physical–chemical mechanism, such as adsorption, desorption or even a chemical reaction including the formation of secondary stable mineral phases. At the present time, bentonite is accepted as the most suitable clay for the engineered barrier in DGRs (Fernandes et al., 2012).

The performance of clay as the main component of the engineered barrier in the DGR has been intensively studied, e.g. its response to intense irradiation (Sorieul et al., 2008), its sorption properties (Fernandes et al., 2012; Stumpf et al., 2001), colloid formation reactions (Bouby et al., 2011) and the connections between sorption chemistry and mechanical compaction (Miller and Wang, 2012). Regarding the clay adsorption properties, recent studies highlight the existence of an additional retention mechanism (Alba et al., 2009a; Trillo et al., 1994). The systematic study of the interaction of the Rare Earth Element (REE) cations, such as La, Lu, Nd, Sm, as actinides chemical analogues, with natural and artificial clay minerals, reveals a reaction mechanism, based on the chemical interaction between the lanthanide cations and the orthosilicate anions of the lamellar structure (Alba and Chain, 2005; Alba et al., 2011). At subcritical conditions, (temperature and pressure), an insoluble and chemically stable phase, $REE_2Si_2O_7$, is generated (Alba et al., 2009b). Therefore, the expected retention capacity of bentonite increases and can provide a stable immobilisation mechanism even when its sorption and swelling capacities fail (Alba and Chain, 2007).

These previous studies are focused on the structural analysis of $REE_2Si_2O_7$, after the hydrothermal reaction between REE cations and clay minerals (Alba and Chain, 2005, 2007; Alba et al., 2009a). More recently, Alba et al. (2011) have quantified the Eu^{3+} immobilisation by a standard saponite, and physical and chemical interactions are analysed. However, the final motivation of these analyses is the study of

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bentonites, since they constitute one of the most recommended materials for the construction of the engineered barrier.

In this work, an evaluation of the retention mechanisms in bentonites is performed. The FEBEX and MX-80 clays are commonly selected as reference materials by various nuclear waste management agencies in the construction of engineered barriers in a potential DGR (Villar et al., 2012).

Therefore, the aims of this study are: i) quantification of the immobilisation power of the bentonites FEBEX and MX-80 in comparison with the pure smectite saponite; ii) completion of a kinetic analysis of the process and a structural analysis of the products of reaction; and iii) verification of the mechanism in a wide range of temperatures, including those where the extent of the reaction is so low that is not possible to detect structural changes.

In order to achieve these objectives, hydrothermal treatments of FEBEX and MX-80 with stable europium are performed in the temperature range between 80 °C and 300 °C. Stable europium was spiked with ^{152}Eu in order to quantitatively compare the reactivity and kinetics of the bentonites to the saponite.

2. Materials and methods

2.1. Clay samples

The FEBEX bentonite was extracted from the Cortijo de Archidona deposit (Almería, Spain). The processing at the factory consisted of disaggregation and gently grinding, drying at 60 °C and sieving by 5 mm (ENRESA, 2000, 2006). The montmorillonite content of the FEBEX bentonite was above 90% (92 ± 3%) (Villar et al., 2012). The MX-80 bentonite was extracted from Wyoming (USA) and was supplied in the form of powder homoionised with sodium (Madsen, 1998). The MX-80 batch used in this investigation was mainly composed of montmorillonite (83%) (Villar et al., 2012). As reference, a purified saponite from the Source Clay Minerals Repository of the University of Missouri (Columbia) was used as reference material (Alba et al., 2001). Table 1 summarises the main clay characteristics (Galunin et al., 2010).

2.2. Eu^{3+} solutions

Two sets of starting solutions of 7.9×10^{-2} M Eu(NO$_3$)$_3$ (^{151}Eu and ^{153}Eu, with 52.2% ^{153}Eu) were prepared: The first solution contained solely stable Eu isotopes; the second solution was enriched with the radioisotope ^{152}Eu (with a half-life of 13.5 years). A volume of 1 ml from a diluted standard solution up to a total activity of 9.8 Bq was added to 35 ml of the former solution, as a compromise for safe radioactive handling and high counting rates for fast measurements. That activity corresponded to 10^{-14} mol of ^{152} Eu. The pH of the two solutions was adjusted to pH = 6.0–6.5, by slowly adding 0.05 M ammonia solution whilst stirring.

2.3. Hydrothermal treatments

Three hundred milligrammes of the powdered samples (Saponite, FEBEX, MX-80) were dispersed in the 40 ml of Eu^{3+} solutions and were heated in a stainless steel reactor (Perdigón, 2002), at the temperatures and times summarised in Table 2. The cells marked with vertical lines correspond to the treatment with a starting solution of 7.9×10^{-2} M Eu(NO$_3$)$_3$, whilst the grey cells correspond to the treatment with a starting solution of 7.9×10^{-2} M Eu(NO$_3$)$_3$ enriched with the ^{152}Eu isotope. The reaction products were collected by filtering using a Millipore filter with 0.45 μm pore diameter, washed with distilled water, and dried in air at 60 °C. The reaction solution and the washing liquid were kept for quantitative analysis of europium by gamma spectroscopy. The solid samples were collected either for gamma (^{152}Eu spiked), or for structural analysis by XRD and SEM/EDX (not spiked with radioactive isotopes).

2.4. Characterisation methods

A Canberra, hyper-pure n-type germanium gamma detector (HPGe), was used for ^{152}Eu gamma spectrometry measurements, in Radioisotopes Service at CITIUS laboratories (Universidad de Sevilla). Counting efficiency was experimentally determined by means of preparing standards spiked with^{152}Eu for the two geometries analysed: filter and cylindrical beaker. Efficiency was verified for both counting geometries using Monte Carlo simulations, through an optimised LABSOCS programme (Hurtado and Villa, 2010).

In the structural study, powered non-^{152}Eu spiked samples were analysed using a Bruker D8 to obtain an X-ray diffraction diagram (XRD), also located at CITIUS laboratories (Universidad de Sevilla). Radiation of Cu, Kα, and Ni filters was chosen, whereby 40 kV, 40 mA, 0.05° 2θ step, and 3 s counting time were the operational parameters. Crystalline phase identification was carried out using the DIFFRAC$^{\text{plus}}$ Evaluation package (©2010 Bruker AXS GmbH, Karlsruhe, Germany).

When crystalline phases could not be identified by XRD, scanning electron microscopy (SEM/EDX) was chosen. Morphologies and chemical compositions were analysed in Microscopy Service in ICMS (CSIC-Universidad de Sevilla) with a SEM-FEG HITACHI S-4800; a scanning electron microscope equipped with an Xflash 4010 (Bruker) for energy dispersive X-ray (EDX) analysis.

3. Results and discussion

3.1. Quantification of the reactivity of clays with Eu^{3+}

Retention of europium in the bentonites was evaluated from the comparison of the initially added radioactive europium with the measurement of the europium in the filter after hydrothermal treatment. Subsequently, milliequivalents of europium per 100 g clay retained in the solid were calculated and displayed for every hydrothermal treatment in Fig. 1, where the amount of europium that would be needed to satisfy the CEC (Cation Exchange Capacity) of the clays (horizontal lines) is also shown.

Predominantly, when the reaction temperature increases, the amount of europium retained in the solid phase increases. At the beginning of the reaction ($t = 0$), the milliequivalents of europium retained by the clays were within the range of the CEC for every temperature, that is, the europium was retained exclusively due to cationic exchange, and no significant chemical reaction took place. At 300 °C, for increasing

Table 1
Characteristics of the clays selected.

Clays	Structural formula	Total charge/u.c.	CEC[d] (meq/100 g)
FEBEX[a]	$(Ca_{0.5}Na_{0.08}K_{0.11})(Si_{7.78}Al_{0.22})(Al_{2.78}Fe^{III}{}_{0.33}Fe^{II}{}_{0.02}Mg_{0.81})O_{20}(OH)_4$	1.19	158.2
MX-80[b]	$(Na_{0.36}Ca_{0.20})(Si_{7.96}Al_{0.04})(Al_{3.1}Mg_{0.56}Fe^{III}{}_{0.18}Fe^{II}{}_{0.16})O_{20}(OH)_4$	0.76	102.1
Saponite[c]	$Na_{0.8}(Si_{7.2}Al_{0.8})(Mg_{5.79}Fe_{0.14})O_{20}(OH)_4$	0.80	103.0

[a] ENRESA, Spain.
[b] CIEMAT, Spain.
[c] Source Clays Repository of the Clay Minerals Society, University of Missouri, Columbia, USA.
[d] Theoretical cation exchange capacity value, mathematically deduced from clay molecular formula.

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