Geochemistry of rare earth elements in acid mine drainage precipitates

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Abstract

Rare earth elements (REE) are known as the lanthanide series (La-Lu) plus yttrium (Y) and scandium (Sc). REE are essential materials for modern industries and especially for green technologies (wind turbines, batteries, lasers, catalysts, etc.). However, despite their high global demand, their supply is limited such that the EU has cataloged it as critical raw materials. In order to ensure the supply of REE in the future, the search for alternative sources of these elements worldwide has been promoted in recent years.

Acid mine drainage (AMD) produced by the Fe-sulphide weathering can effectively leach Fe, Al, SO4, and REE from the host rock. This can lead to high concentrations of these liberated species in the affected waters. Thus, the REE concentrations in AMD can be between two and three orders of magnitude higher than natural waters, as such it can be considered as a complementary source of REE recovery. The increase of pH in AMD by mixing neutral waters results in the precipitation of iron oxy-hydroxysulfate (schwertmannite) from pH 3-3.5, and aluminum (basaluminite) from pH 4-4.5 in the river channels. This process may be accompanied by REE scavenging.

Due to its acidity and high metal load, acid mine drainage presents a major environmental problem worldwide, therefore, different treatment systems have been developed to minimize its impact. Disperse Alkaline Substrate (DAS) passive remediation system neutralizes AMD by dissolving calcite, and allowing the sequential precipitation of schwertmannite and basaluminite in separated layers, where REE are preferably retained in the basaluminite-enriched waste. Despite this, there are still no studies describing the adsorption of REE on both basaluminite and schwertmannite in these environments.

The REE scavenging mechanism is studied by adsorption on synthetic minerals of basaluminite and schwertmannite as a result of variation to the both the pH and sulfate concentration. A thermodynamic adsorption model is proposed based on experimental results in order to predict and explain the REE mobility in AMD mixtures with neutral waters and in a passive treatment system.

Basaluminite and schwertmannite have a nanocrystalline character. Further, schwertmannite has been observed to transform into goethite on weekly timescales, resulting in sulfate release. However, there is a gap of knowledge about basaluminite stability at variable sulfate concentration and pH and its possible transformation to other more crystalline Al-minerals. In this study, basaluminite local order at different pH values and dissolved sulfate concentrations was characterized. Results demonstrate that basaluminite can transform to nanoboehmite in weeks under circumneutral pH. However, the presence of sulfate can inhibit this transformation.

Separate adsorption experiments on both basaluminite and schwertmannite were performed with two different concentrations of SO_4 while varying the pH (3-7). Results show that the adsorption is strongly dependent on pH, and to a lesser extent on sulfate concentration. Lanthanide and yttrium adsorption is most effective near pH 5 and higher, while that of scandium begins around pH 4. Due to the high concentrations of sulfate in acidic waters, the predominant aqueous REE species are sulfate complexes (MSO_4^+). Notably, $Sc(OH)^{2+}$ represents a significant proportion of aqueous Sc. , A surface complexation model is proposed in which predominant aqueous species (M^{z+}) adsorb on the mineral surface, XOH, following the reaction:

$$\mathrm{M^{z+} + nXOH = (XO)_nM^{z-n} + nH^+}$$

The adsorption of the lanthanides and yttrium occurs through the exchange of one and two protons from the basaluminite and schwertmannite surface, respectively, with the aqueous sulfate complexes. The sorbed species form monodentate surface complexes with the aluminum mineral and bidentate with the iron mineral. In the case of Sc, the aqueous species $ScSO^{4+}$ and $Sc(OH)^{2+}$ form bidentate surface complexes with both minerals. EXAFS analysis of the YSO_4^+ complex adsorbed on the basaluminite surface suggests the formation of a monodentate inner sphere complex, in agreement with the proposed thermodynamic model.

Once the surface complexation model was validated, it was used to asses and predict the REE mobility in passive remediation systems and acidic water mixing zones with alkaline inputs from the field. The REE are preferentially retained in basaluminite-rich waste during passive remediation due to its sorption capacity between pH 5-6. In contrast, schwertmannite waste contains very little REE because the formation of this mineral occurs at pH lower than 4, which prevents REE adsorption. Further, Sc may be scavenged during schwertmannite precipitation as a result of this low pH

The model correctly predicts the absence of REE in schwertmannite precipitates and the enrichment of the heavy and intermediate REE with respect to the light REE in basaluminite precipitates collected in the water mixing zones. However, there is a systematic overestimation of the fractionation of rare earths in basaluminite precipitate. This inaccuracy is mainly due to the fact that the mineral precipitation and adsorption are not synchronous process, while basaluminite precipitates from pH 4, REE adsorption occurs at higher pH values, between 5 and 7, when the water mixture reaches these values and a fraction of the particles have been dispersed.

Resumen

Las tierras raras (en inglés *rare earth elements*, REE) son conocidas como el conjunto de la serie de los lantánidos (La-Lu), itrio (Y) y escandio(Sc). Las tierras raras son materiales indispensables para las industrias modernas y en especial para las tecnologías verdes (aerogeneradores, baterías, láseres, catalizadores, etc.). Sin embargo a pesar de su gran demanda mundial, su abastecimiento es limitado, por lo que han sido catalogadas por la UE como materias primas críticas (Critical Raw Materials). Con el objetivo de asegurar el abastecimiento de REE en el futuro, en los últimos años se ha promovido la búsqueda de fuentes alternativas de estos elementos en todo el mundo.

El drenaje ácido de mina (en inglés *acid mine drainage*, AMD) producido por la meteorización de sulfuros de Fe, tiene un alto poder de lixiviación de las rocas, por lo que las aguas afectadas adquieren elevadas concentraciones en disolución de Fe, Al, SO_4 y otros metales, como las REE. Así, las concentraciones de REE en AMD son entre dos y tres órdenes de magnitud superiores al resto de las aguas naturales y pueden suponer una fuente complementaria de recuperación de REE. El aumento de pH del AMD por mezcla con aguas neutras da lugar a la precipitación en los cauces de los ríos de oxy-hidroxisulfatos de hierro (schwertmannita), a partir de pH 3-3.5, y de aluminio (basaluminita), a partir de pH 4-4.5; acompañado de la eliminación de las tierras raras.

Debido a su acidez y carga metálica, el drenaje ácido de mina presenta un problema medioambiental de primera magnitud, por lo que se han desarrollado diferentes sistemas de tratamiento para minimizar su impacto. El sistema de tratamiento pasivo *Disperse Alkaline Substrate* (DAS) produce la neutralización de las aguas ácidas por la disolución de la calcita presente en el sistema, permitiendo la precipitación secuencial, de schwertmannita y basaluminita. Las tierras raras quedan retenidas preferentemente en el residuo enriquecido en basaluminita. A pesar de ello, aún no existen estudios que describan la adsorción de tierras raras tanto en basaluminita como schwertmannita en estos ambientes.

En esta tesis se estudia el mecanismo de retención de las tierras raras mediante adsorción en minerales sintéticos de basaluminita y schwertmannita, en función del pH y del contenido de sulfato disuelto. Con los resultados experimentales obtenidos, se propone un modelo termodinámico de adsorción para predecir y explicar la movilidad de las tierras raras observada en mezclas de AMD con aguas neutras y en un sistema de tratamiento pasivo.

La basaluminita y la schwertmannita presentan un carácter nanocristalino. Es conocido que la schwertmannita se transforma en goethita en semanas, liberando sulfato. Sin embargo, nada se sabe de la basaluminita y su posible transformación a otros minerales de Al más cristalinos. De este modo, la caracterización del orden local de la basaluminita a diferentes valores de pH y sulfato se expone en primer lugar. Dependiendo del pH y el sulfato en disolución, la basaluminita se transforma en diferentes grados a nanoboehmita en semanas, pero tiende a estabilizarse con la presencia de sulfato en solución.

Los experimentos de adsorción en basaluminita y schwertmannita con diferentes concentraciones de SO_4 realizados para cada mineral y en rangos de 3-7 de pH han demostrado que la adsorción es fuertemente dependiente del pH, y en menor medida del sulfato. La adsorción de los lantánidos y del itrio es efectiva a pH 5, mientras que la del escandio comienza a pH 4. Debido a las altas concentraciones de sulfato en aguas ácidas, las especies acuosas predominantes de las tierras raras son los complejos con sulfato, MSO_4^+. Además del complejo sulfato, el Sc presenta importantes proporciones de $Sc(OH)^{2+}$ en solución. En función de la dependencia del pH y de la importancia de la especiación acuosa, se propone un modelo de complejación superficial donde la especie acuosa predominante (M^{z+}) se adsorbe a la superficie libre el mineral, XOH, cumpliendo la siguiente reacción:

$$\mathrm{M^{z+} + nXOH = (XO)_nM^{z-n} + nH^+}$$

La adsorción de los lantánidos y del itrio se produce a través del intercambio de uno o dos protones de la superficie de la basaluminita o de la schwertmannita, respectivamente, con los complejos sulfato acuoso, formando complejos superficiales monodentados con el mineral de aluminio y bidentados con el de hierro. En el caso del Sc, las especies acuosas $ScSO_4^+$ y $Sc(OH)^{2+}$ forman complejos superficiales bidentados con ambos minerales. Complementando el modelo propuesto, el análisis de EXAFS del complejo YSO_4^+ adsorbido en la superficie basaluminita sugiere la formación de un complejo monodentado de esfera interna, coincidiendo con el modelo termodinámico propuesto.

El modelo de complejación superficial, una vez validado, ha permitido evaluar y predecir la movilidad de REE en los sistemas de tratamiento pasivos y en zonas de mezcla de aguas ácidas con aportes alcalinos estudiados en el campo. La preferente retención de las tierras raras en la zona de la basaluminita precipitada en los sistemas de tratamiento pasivo ocurre por adsorción de las mismas a pH entre 5-6. La ausencia de tierras raras en la zona de schwertmannita se debe al bajo pH de su formación, inferior a 4, que impide la adsorción de las mismas. Sin embargo, debido a su menor pH de adsorción, una fracción de Sc puede quedar retenida en la schwertmannita.

El modelo también predice correctamente la ausencia de REE en los precipitados de schwertmannita y el enriquecimiento de las tierras raras pesadas e intermedias respecto a las ligeras en los precipitados de basaluminita recogidos en el campo en las zonas de mezcla de aguas. Sin embargo, se ha observado una sistemática sobreestimación del fraccionamiento de las tierras raras en los precipitados de basaluminita. Este hecho se debe principalmente a que la precipitación del mineral no ocurre de forma síncrona con la adsorción, precipitando la basaluminita a partir de pH 4 y adsorbiendo tierras raras a pH más altos, entre 5 y 7, cuando las partículas sólidas han sido parcialmente dispersadas.

1 Introduction

Lanthanide series (from La to Lu) plus scandium (Sc) and yttrium (Y) are referred to as Rare Earth Elements (REE) according to recommendation by the International Union of Pure and Applied Chemistry (Connelly et al., 2005). They occur in nature as trivalent species with the exception of Ce and Eu which can also appear as Ce^{4+} and Eu^{2+}. Lanthanides group can be arbitrarily divided into light (LREE: La to Nd), medium (MREE: Sm to Gd) and heavy (HREE: Tb to Lu). Due to it atomic size similarity, Y is often considered with HREE, whereas Sc has been commonly set aside the group by its small ionic radius. Their similar atomic structure and chemical properties as well as the small differences among the elements in the group have traditionally converted their partition between water and minerals as tracers of geochemical processes (Henderson, 1984; McLennan, 1989; Elderfield et al., 1990; Chakhmouradian and Wall, 2012, among many others). Beyond their importance as geochemical tracers, in the last two decades, there has been an increasing interest in REE due to their higher demand by modern technology and industry, such as manufacturing in permanent magnets, batteries, light emitting diodes and alloys, among other technological advancements. Their low supply due to limited REE mining to find new sources of these elements (Alonso et al., 2012; Hatch, 2012) and where China dominates more than 90% of worldwide production (U.S. Geological Survey (USGS), 2019) has led to consider REE as Critical Raw Materials, boosting searches for alternative sources of REE worldwide (Alonso et al., 2012; Hatch, 2012; Massari and Ruberti, 2013). Moreover, although REE have been considered of minor environmental concern, due to their common use in modern industry, some toxicological studies suggest that they could have a pathogenic potential (Zhuang et al, 1996; Dai et al., 2002; Pagano et al., 2015; Roncati et al., 2018). Therefore, knowing the mobility constraints of REE in natural waters, and particularly in AMD is a target of interest.

Acid Mine Drainage (AMD) is one of the most widespread pollution affecting watersheds and ecosystems (Nordstrom, 2011; Nordstrom et al., 2015). However, the REE concentrations in AMD, including Sc, are several orders of magnitude higher than the rest of surface waters and could be a future supplementary source of some highly valuable REE (Ayora et al., 2016; Stewart et al., 2017; Zhang and Honaker, 2018). AMD also contains high concentrations of toxic elements in addition to REE, and represents a very important environmental threat that requires remediation. In mine operations, the active treatments of AMD are mainly based on its neutralization with alkaline reagents, usually limestone, sodium carbonate or ammonia (Evangelou and Zhang, 1995; Coulton et al., 2003). This treatment produces high amounts of an sludge formed by a mixture of Fe(III) and Al-sulfate-hydroxides which disposal represents a major operating cost for coal and metal mining operations (Ackamn, 1982; Viadero et al., 2006). Differently, the passive remediation systems, which have been developed extensively in recent decades, allow the AMD neutralization generating lower amounts of solid waste precipitates by driving AMD through a permeable system filled with grained limestone (Hedin et al., 1994; Cravotta and Trahan, 1999; Ayora et al., 2013). Along the process, a sequential precipitation of mainly schwertmannite ($Fe_8O_8(OH)_6SO_4$) and basaluminite ($Al_4SO_4(OH)_{10}{\cdot}5H_2O$) waste occurs in differentiated layers (Caraballo et al., 2011a). There, lanthanide and Y have been proved to be entirely retained in the basaluminite-enriched solid and nearly absent in Fe-enrich solids (Ayora et al., 2016; Zhang and Honaker, 2018). Therefore, likewise in natural attenuation of AMD affected waters, a detailed understanding of the mechanism responsible for selective REE scavenging by basaluminite and/or schwertmannite, is necessary. Moreover, the passive treatment systems can work for several months to years with a constant pH evolution, so potential transformation of the minerals can be expected. Schwertmannite transformation to goethite with time has well characterized (Schwertmann and Carlson, 2005; Acero et al., 2006; Burton et al., 2008; Cruz-Hernández et al., 2018). Basaluminite has reported to coexist with nanocrystals of $Al(OH)_3$ in aluminum precipitates formed in pit lakes, that suggest basaluminite partial transformation to nanoboehmite or gibbsite (Sánchez-España et al., 2016). However, no studies regarding basaluminite stability are present in the literature. Thus, a detailed characterization of the stability of basaluminite at different solution pH values becomes essential previous to study sorption mechanisms.

The REE distribution pattern normalized to the North American Shale Composite (NASC) has been used to prove the impact of Acid Mine Drainage (AMD) in groundwater, rivers and estuarine environments (Vallejo et al., 2012; Grawunder et al., 2014; Morgan et al., 2016; Bonnail et al., 2017; Li and Wu, 2017). It is generally recognized that the REE concentration in water is largely controlled by solid surface and aqueous solution chemistry (Quinn et al., 2006a; Quinn et al., 2006b and refences therein). Besides, REE fractionation between minerals and AMD has been studied since the early 1990s as rock weathering (Auqué et al., 1993; Gimeno et al., 1999) and in mining areas (Gammons et al., 2003). Verplanck et al. (2004) observed REE scavenging from AMD by hydrous ferric oxides as the pH increased to 5.1 due to the water mixing in two AMD streams. The authors attributed the REE removal to sorption onto Fe(III) precipitates. Similar REE behavior was detected by Gammons et al. (2005a) in a mountain stream affected by AMD. Samplings conducted in at three stations: upstream station (pH 3.3), intermediate (pH 5.5) and downstream (pH 6.8), showed that REE remained in solution in the two first stations. The removal at high pH was interpreted as sorption on suspended particles of undifferentiated Fe and Al hydroxides. Concomitant to the previous study, (Gammons et al., 2005b) collected samples along 40 km along the Patagonian Agrio river, which is initially acid due to volcanic discharges. Most of the decrease in REE load occurred immediately downstream of the confluence with a tributary that increased the pH of the Rio Agrio from 4.3 to 6.1. Again, these authors proposed sorption of REE on hydrous Al oxides as the mechanism responsible for the loss of REE with the drop in Al concentration. Similar observations were made by Ferreira da Silva et al. (2009) in the AMD of the Lousal mine (S. Portugal), where a decrease in REE concentrations was observed as the pH increased from 3 to 6 due to the confluence with a tributary stream. All the aforementioned studies suggested sorption mechanisms on Fe and Al hydroxysulfates as responsible for REE retention. Therefore, interaction with the most relevant solids formed in AMD environments, schwertmannite and basaluminite, is expected to play a relevant role in the characteristic water lanthanide distribution pattern.

Laboratory experiments of sorption and coprecipitation of REE onto ferric and manganese oxides/hydroxides have previously demonstrated the key role of pH in the geochemical mobility of REE (Bau, 1999; Ohta and Kawabe, 2000; Ohta and Kawabe, 2001; Quinn et al., 2004; Quinn et al., 2006a). REE are removed from solution as the pH increases from 4 to 9. In addition to pH, aqueous speciation is also an important factor that has been driven its attention in REE fractionation in marine environments. Thus, the formation of strong carbonate complexes with heavy REE (HREE) at neutral pH values prevents their sorption by ferric and manganese oxides. As a result, these solids show patterns with light REE (LREE) enrichment (Byrne R.H., 1990; Koeppenkastrop and De Carlo, 1992; Sholkovitz, 1995; Byrne and Sholkovitz, 1996; Kawabe, 1999a; Kawabe, 1999b).

In order to predict REE sorption behavior, surface complexation models (SCM) have developed to describe the sorption of some lanthanides (Yb, La, Eu) onto hematite and amorphous ferric oxides/hydroxides (Marmier et al., 1997; Rabung et al., 1998; Marmier et al., 1999; Quinn et al., 2006b; Quinn et al., 2006a; Estes et al., 2013; Pourret and Davranche, 2013; Liu et al., 2017). In contrast, aluminum phases are not as common as ferrous oxide phases, and there are few studies related to the REE uptake for aluminum oxides. For example, the uptake of Eu and Yb by alumina (Al_2O_3), at varying pH, ionic strength and acid fulvic concentrations, has been studied by soil scientists as an analogue for actinides in nuclear waste disposal (Xiangke et al., 2000). Experimental sorption edges for Yb and Eu(III) onto alumina were reproduced using SCM by Marmier et al., (1997) and Rabung et al. (2000), respectively.

In all these works, the REE scavenging is mainly explained by the sorption of free REE ions or their hydrolyzed species onto a solid surface with high dependence on pH. In addition to pH, sulfate has the potential to change the sorption behavior of REE and other metals in AMD systems. The presence of sulfate is ubiquitous in AMD systems, usually with concentrations reaching up to several grams per liter. Indeed, aqueous sulfate complexes are predominant in AMD over a wide range of pH values (Gimeno Serrano et al., 2000; Verplanck et al., 2004), and sulfate is a major constituent of the Fe and Al solid phases, schwertmannite and basaluminite. Similar to REE-carbonate speciation in seawater, sulfate complexes may explain REE fractionation in the solids precipitated from AMD environments. Therefore, sulfate is expected to play a major role in aqueous-solid partitioning. Despite their key role in AMD geochemistry, nor experimental and modeling studies of REE sorption on these two minerals have been investigated neither the role of pH and aqueous sulfate in REE sorption have quantitatively assessed.

1.1 Objectives

The main goal of this work is to understand the behavior of REE in AMD environments and its retention mechanism in basaluminite and schwertmannite, the two main minerals that precipitates in AMD neutralization processes.

Although both basaluminite and schwertmannite precipitates are common in AMD areas, the structure and stability of the former mineral has been less studied, so previous to sorption experiments, ageing experiments of synthetic basaluminite in two different aqueous solutions has performed (paper 1). The objectives from this part are:

- To characterize the local structure of pure synthetic basaluminite and to compare it with amorphous $Al(OH)_3$ and nanoboehmite.
- To assess the role of pH and dissolved sulfate in the stability of synthetic basaluminite along the time.
- To understand how its metastable character its transformation to more crystalline phases can affect its local structure.

Based on previous sorption experiments of REE onto both ferric and aluminum oxides/hydroxides, sorption of REE onto basaluminite and schwertmannite are carried out at different pH and sulfate concentrations (papers 2 and 3). The objectives from this part are:

- To assess the sorption capacity of each mineral as a function of pH and two different sulfate concentrations.
- To characterize the REE fractionation in these two minerals and compare with those observed in ferric/aluminum oxides/hydroxides.
- To develop a thermodynamic surface complexation model from experimental sorption results with higher sulfate concentration and 1g/L solid:liquid ratio.

- To validate the model proposed with other experimental sorption results performed at lower sulfate concentrations and different solid:liquid ratios for each mineral.

The study of the thermodynamic model was complemented with synchrotron-based techniques in order to describe at atomic scale the sorption mechanism onto basaluminite (paper 4). This work was performed only with yttrium element, rather than with all REE since EXAFS is an atomic-selective technique. The objectives from these parts are:

- To characterize the local structure of YSO_4^+ aqueous specie since the sorption model describes the REE sorption in terms of aqueous REE-sulfate complex onto the mineral surface. The study was performed using experimental EXAFs and PDF analyses and supported by the results of AIMD simulations.

- To define at atomic scale the surface complex formed by the aqueous specie YSO_4^+ and the surface of synthetic basaluminite. The characterization was carried out performing EXAFS and PDFs analyses of synthetic solids.

- To determine the solid speciation of basaluminite-rich waste samples recovered from a passive remediation system performed at laboratory scale, comparing the local structure of these samples with different Al-precipitates, such as basaluminite and boehmite doped with Y and YSO4.

A passive remediation treatment at column scale was performed in order to assess the mobility of REE in the system, focusing on the geochemistry of pore water and the of the solid waste (paper 3). The specific objectives of this part are:

- To reproduce the aqueous REE evolution in pore water through column depth and along the time.

- To compare the profile of minerals precipitation and the mobility of REE in the model with the profile of REE in solid waste from column experiments.

- To explain the preferential retention of lanthanides and yttrium in basaluminite-rich solid waste.

The last part of the thesis is focused on the description of REE mobility in two AMD field sites of Spain (Odiel and Tinto catchments, SW Spain and Arroyo del Val, NE Spain) (paper 5). The objectives of this part are:

- To describe the REE mobility in AMD mixing with alkaline inputs from aqueous samples recovered from the field sites.

- To describe the solids precipitated in the mixing zones and the REE patterns observed in the solids.

- To reproduce the REE patterns analyzed in the solids recovered from AMD affected waters, using the aqueous data and the thermodynamic model.

2 Results

2.1 Local structure of basaluminite after ageing in solutions at different pH values and sulfate concentrations.[1]

The results of fast ageing experiments of suspensions of 1g/L basaluminite in 0.01 M $NaNO_3$ showed clear SO_4:Al and H^+:Al linear correlations with ratios of 1.40 and -0.19, respectively. The saturation indices indicated that at the beginning, the solution was undersaturated with respect to basaluminite, gibbsite and boehmite but quickly reached supersaturation with respect to these phases. These correlations are explained as an incongruent basaluminite dissolution with the subsequent Al hydrolysis and $Al(OH)_3$:

$$\mathrm{Al_4(SO_4)_{1.25}(OH)_{9.5}} + 0.17\ \mathrm{H^+} \rightarrow 0.89\ \mathrm{Al^{3+}} + 1.25\ \mathrm{SO_4^{2-}} + 3.11\ \mathrm{Al}(OH)_{3(s)} + 0.17\ H_2\mathrm{O} \qquad (2.1)$$

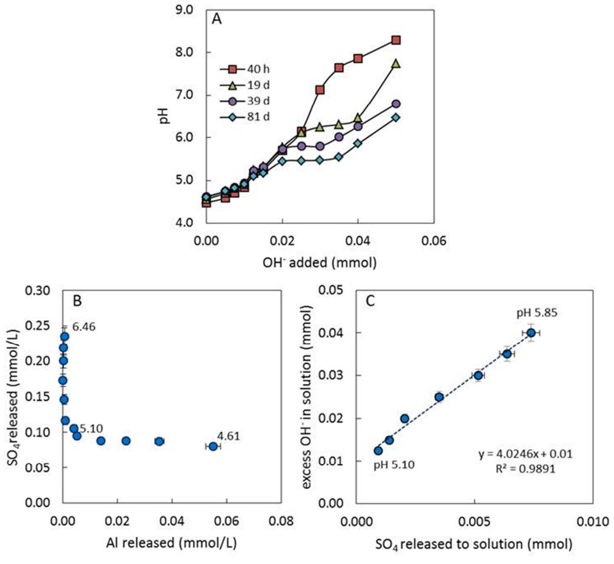

Figure 2.1 (A) Evolution of pH for the suspensions with different initial pH values. (B) Aluminium and SO_4 evolution of the different suspensions after 81 days of ageing. The values depicted inside are the final pH values. (C) Correlation between the OH^- excess and SO_4 concentration for the suspensions with higher pH values.

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[1] *This part of the thesis is based on the article Lozano et al., 2018. Chem. Geol. 496, 25-33.*

In the slow ageing experiments, beyond the first 48 hours and after OH^- addition, a decrease in the pH was observed and the decrease was more accentuated when no sulphate was added to the initial suspensions (Figure 2.1). For pH values higher than 5.1, the Al in solution was below the detection limit, but he molar ratio between the SO_4 released and the excess OH^- was 4. This result can be explained by a sequence of chemical reactions involving the dissolution of basaluminite and the formation of nanoboehmite and natroalunite, $NaAl_3(SO_4)_2(OH)_6$, according to the process reaction:

$$\begin{aligned} &5Al_4(SO_4)(\mathrm{OH})_{10}\cdot 5\mathrm{H_2O} + 2\mathrm{Na} + 4\mathrm{OH}^- \\ &\qquad \rightarrow 2\mathrm{NaAl_3(SO_4)_2(OH)_6} + 14\mathrm{AlOOH} + \mathrm{SO_4^{2-}} + 39\mathrm{H_2O} \end{aligned} \quad (2.2)$$

Owing to the high amount of sulphate added, such a variation in sulphate concentration was not observed in the experiments where Na_2SO_4 was added to the initial suspensions. However, the structure factors clearly showed that boehmite peaks appeared in the solids from the experiments with higher initial pH values (Figure 2.2). The differential PDFs, generated by subtracting the PDF of pure basaluminite from each sample, show a negative peak of increasing intensity at 1.49 Å, corresponding to the release of sulfate from samples as the pH increases, and a transition to more crystalline phase. Similar trends were observed in the differential PDFs of the experiment with added sulfate, although with less negative peaks at 1.49 Å. From these observations, a transformation of basaluminite to nanoboehmite with time can be inferred. Thus, the experiments demonstrated that basaluminite is a metastable precipitate that can transform into more stable Al hydroxide phases, when ageing in/near neutral waters. This process can affect the behaviour of trace elements, such as REE, that could be adsorbed onto its surface.

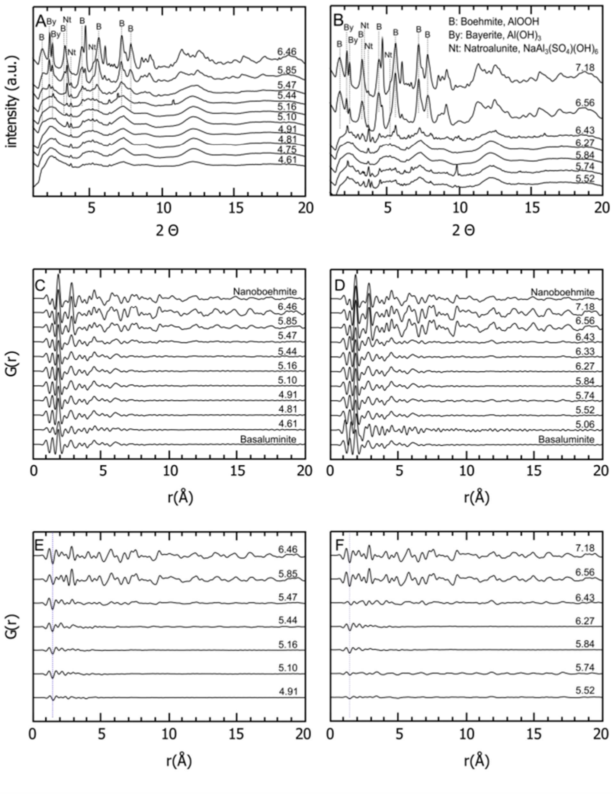

Figure 2.2 Structure factors with Q converted to 2θ for the solid samples equilibrated and aged during 81 days in the absence of sulfate (A) and with an initial sulfate content (B). The wavelength of the X-rays used was of λ=0.181 Å. (C, D) PDFs of the aged solids and synthetic nanoboehmite and basaluminite for the experiment in the absence of sulfate and with initial sulfate, respectively. (E, F) Differential PDFs the two both experiments. The vertical dotted line indicates the position of the S-O bond. Negative peaks reflect the decrease in the sulfate content in the solids.

2.2 Sorption experiments[2]

Sorption experiments of REE with synthetic basaluminite and schwertmannite was performed as a function of pH and sulfate concentrations. Two set of batch sorption experiments were performed with each mineral. For the first set, a solution of 1mg/L of each REE with 20 mM SO_4 was used with the two minerals. For the second set, a solution of 1 mg/L of each REE without sulfate was used with basaluminite, and a solution of 1 mg/L of each REE and 2 mM SO_4 was used with schwertmannite. The two set of experiments covered a pH range of 4-7 with basaluminite and 3-7 with schwertmannite, respectively. The sorption experiments were carried out for 6 hours since maximum sorption was reached for this time and to minimize a possible basaluminite transformation more crystalline Al-phases at high pH values, as showed in the results of basaluminite ageing experiments. The sorbed fractions were calculated as follows:

$$\text{Sorbed fraction } = \frac{[\text{REE}]_{\text{initial}} - [\text{REE}]_{\text{final}}}{[\text{REE}]_{\text{initial}}} \qquad (2.3)$$

where [REE] is the concentration of each REE. The initial concentration was measured in the stock solution and the final concentration after the experiment. The distribution coefficient, K_D (L/kg), for each REE was calculated from the [REE] sorbed onto the solid per the final [REE] remaining in solution and normalized per the solid:liquid ratio:

$$K_D = \frac{[\text{REE}]_{\text{initial}} - [\text{REE}]_{\text{final}}}{[\text{REE}]_{\text{final}}} \cdot \frac{V_{\text{solution}}}{M_{\text{solid}}} \qquad (2.4)$$

The XRD patterns of the synthetic solids confirmed that the minerals were pure and the BET indicated a surface area of 68 m^2/g and 173 m^2/g for basaluminite and schwertmannite, respectively. The site densities for basaluminite were therefore calculated from crystal structure of felsöbányaite, as basaluminite presents similar local order, as stated by (Farkas and Pertlik, 1997; Carrero et al., 2017). Similarly, the site density for schwertmannite was obtained from crystal structure of proposed by (Fernández-Martínez et al., 2010). The averaged surface sites for the two solids calculated for each 100, 010 and 001 faces, are 4.6 and 4.7 nm^{-2} for basaluminite and schwertmannite, respectively. These values will be used for model validation in below sections.

2.2.1 Sorption edges

All final solutions for the four sets of experiments were subsaturated with respect to the REE hydroxides and, therefore, no REE hydroxide precipitation was expected. All the final solutions from experiments with basaluminite except one were supersaturated with respect to basaluminite (Saturation indices between 0.06 and 1.3). Small amounts of dissolved sulfate were present in the final solutions without initial sulfate. There, the amount of dissolved sulfate increased from 0.1 to 0.9 mM with increasing pH. This is interpreted as the exchange of sulfate from basaluminite with OH groups from the solution (Lozano et al., 2018). The experiments without initial sulfate will be hereafter noted as 0.5 mM SO4, indicating the mean value.

The final solutions from experiments with schwertmannite were also subsaturated with respect to schwertmannite and almost in equilibrium with respect to goethite. Schwertmannite exists in a metastable phase that transforms to goethite over weeks at different pH values (Schwertmann and Carlson, 2005; Acero et al., 2006; Burton et al., 2009). However, the presence of sulfate in solution

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[2] *This part of the thesis is based on the articles Lozano et al., 2019a. Geochim.Cosmochim. Acta 258, 50-62, and Lozano et al., 2019c. App. Geochem. Submitted.*

delays this transformation (Regenspurg and Peiffer, 2005), and no goethite was detected by XRD in schwertmannite solids after the sorption experiments.

The experimental results for the two set of experiments carried out with each mineral showed that REE sorption is highly dependent on pH, increasing with it (Figure 2.3). Sorption of lanthanides and yttrium is effective from around pH 5 for both minerals. Scandium, however, behaves different, being sorbed from around pH 4. The experimental results of the sets with lower amounts of sulfate, 0.5 mM SO_4 with basaluminite and 2 mM SO_4 with schwertmannite, showed lower sorption fraction at the same pH valued. The sorption decrease at lower sulfate content in solution suggests that sulfate may play a role in sorption process. The sorption also differs among the REE. At a specific pH value, the fraction of HREE (Lu or Y) sorbed in the solid is higher with respect to LREE (La).

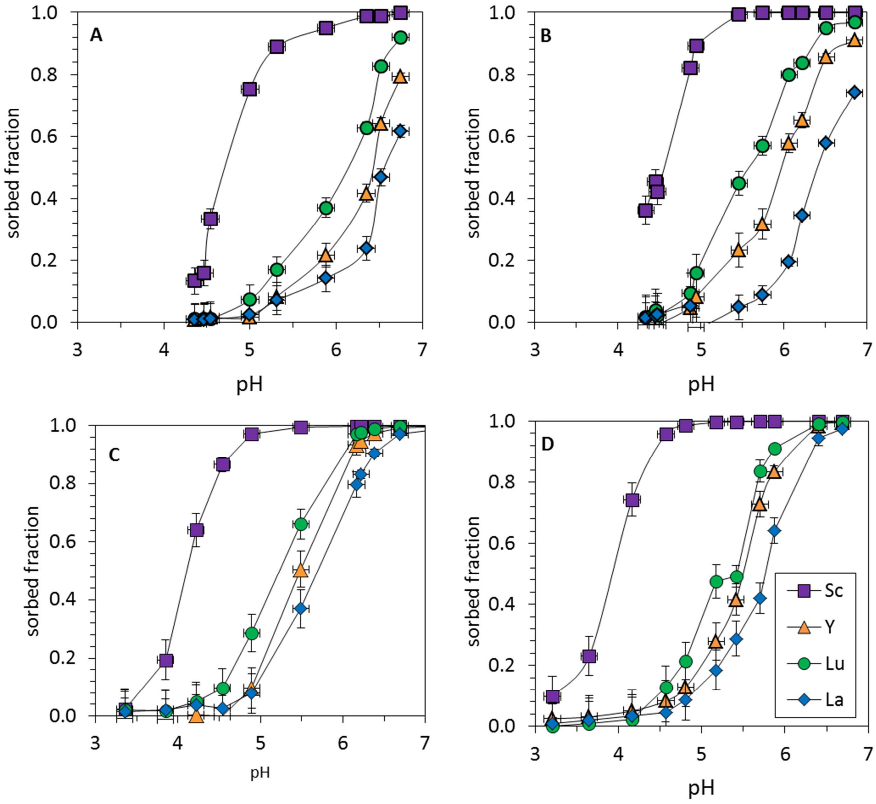

Figure 2.3 Experimental results (symbols) of four REE into 1g/L synthetic A, B) basaluminite and B,C) schwertmannite in suspensions of 20 mM SO_4 (A,C) and 0.2 and 2 mMSO_4 (B, D, respectively).

2.2.2 REE fractionation patterns

The distribution coefficients (K_D) for both sets of experiments were calculated as described in Eq. (2) and are shown in Figure 2.4. From pH 5 in basaluminite and pH 4.5 in schwertmannite upwards, the log K_D patterns reflect HREE enrichment relative to LREE in the solid phases varying close to 1 unit of log K_D along the lanthanide series in both sets of experiments and for both minerals, although less HREE enrichment is observed for schwertmannite. Similar patterns were observed by Bau (1999) for their coprecipitation experiments of REE and Fe at low pH values. Similar relative enrichment in heavy lanthanides was observed in aluminum and ferric hydroxides precipitated in acidic rivers after their neutralization via mixing with alkaline tributaries (Gammons et al. 2003, 2005; Verplanck et al., 2004) and in REEs coprecipitated with synthetic Fe(III)-hydroxides (De Carlo et al., 1998; Quinn et al., 2004).

The REE fractionation patterns showed four convex segments from La to Nd, from Nd to Gd, from Gd to Ho and from Ho to Lu, corresponding to the M-type tetrad effect (Masuda et al., 1987; Bau et al., 1996). However, these results contrast with those described in seawater environments, where a preferential LREE enrichment in the Fe oxides has been observed. Stable aqueous carbonate complexes with HREE formed in marine environments to prevent their adsorption (Koeppenkastrop and De Carlo, 1992; Kawabe et al., 1999b). In acid mine waters, however, sulfate complexes are the dominant aqueous species, while carbonate complexes are only relevant at pH values higher than 6.5.

More specifically, patterns for basaluminite solids showed a small positive Ce only at low pH and low SO_4 concentration, possibly due to a partial/total oxidation of Ce^{3+} to Ce^{4+}, as Koeppenkastrop and De Carlo (1992) proposed for the positive anomalies observed in vernadite. However, this anomaly is not as evident as in the former mineral in the two patterns obtained for schwertmannite solids. Similarly, precipitates obtained after neutralizing acid mine waters with high sulfate concentration did not show this anomaly (Verplanck et al., 2004), which suggests that sulfate may inhibit Ce oxidation due to sulfate complexation. According to its ionic radius, Y is commonly displayed between Dy and Ho, where it presents a negative anomaly in both precipitates, as evidenced by the K_D^Y/K_D^{Dy} and K_D^Y/K_D^{Ho} ratios below unity. The Y anomalies in amorphous Fe(III)-hydroxides were attributed to covalent interactions with the Fe solids (Quinn et al., 2004).

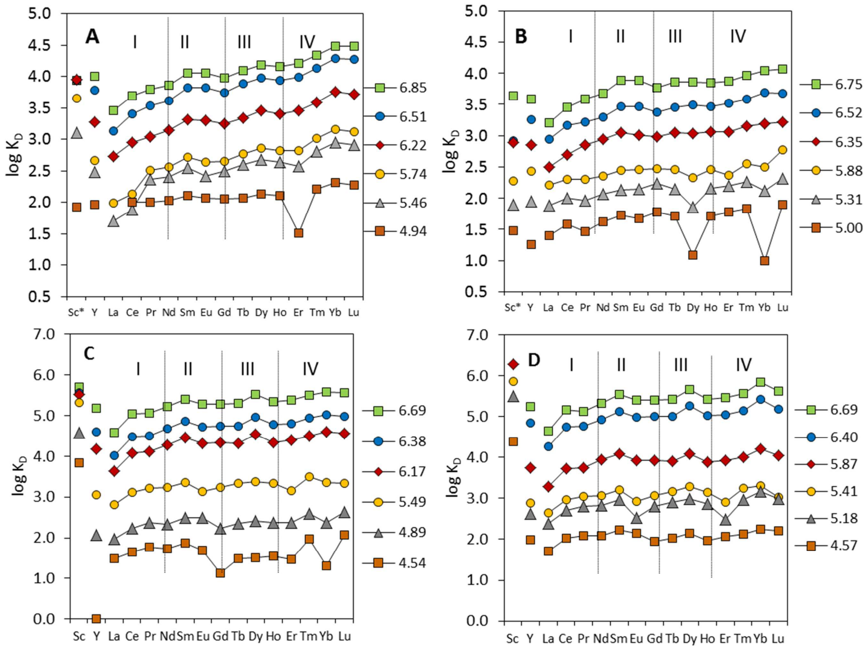

Figure 2.4 Log K_D values at different pH values showing the lanthanide M-type tetrad effect: (A,B) on basaluminite; (C,D) on schwertmannite and in solutions with 20 mM SO_4; (A,C) and with 0.5 and 2 mM SO_4 (B,D). (Sc = log K_D^{Sc}-2)*

Basaluminite precipitates from the experiments with low SO_4 concentration, displayed negative Yb and Dy anomalies that attenuated as the pH increased. These anomalies were absent at high sulfate concentrations. In contrast, at higher sulfate concentrations, a negative Er anomaly was showed at lower pH values, that was attenuated when pH increased and this Er anomaly was not observed with lower sulfate content. These anomalies are not previously described in similar sorption/coprecipitation experiments using amorphous ferric hydroxides (Bau, 1999; Ohta and Kawabe, 2000; Quinn et al., 2006a). Finally, the negative Gd and Yb anomalies showed in schwertmannite precipitates at lower pH values from the experimental set with 20 mM SO_4 were not previously reported in the literature for similar experiments (Bau 1999; Quinn et al., 2006a,b) and are attributed to analytical errors.

2.3 Structure of YSO_4^+ aqueous complex and surface complex onto basaluminite[3]

2.3.1 Geometry of the aqueous YSO_4^+ complex

The major aqueous MSO_4^+ complexes formed in high sulfate concentration solutions, simulating AMD environments are expected to sorb in the surface of basaluminite and schwertmannite. Thus, a structural characterization of the aqueous complex is required previous to a local description of MSO_4^+ attached to the surface of these minerals. Extended X-ray Absorption spectroscopy was used to study the YSO_4^+ combined with pair distribution function (PDF) analyses and ab-initio molecular dynamics simulations (AIMD). Yttrium was the selected element due to its chemical characteristics with other HREEs and since it was of the most concentrated elements in waste samples analyzed.

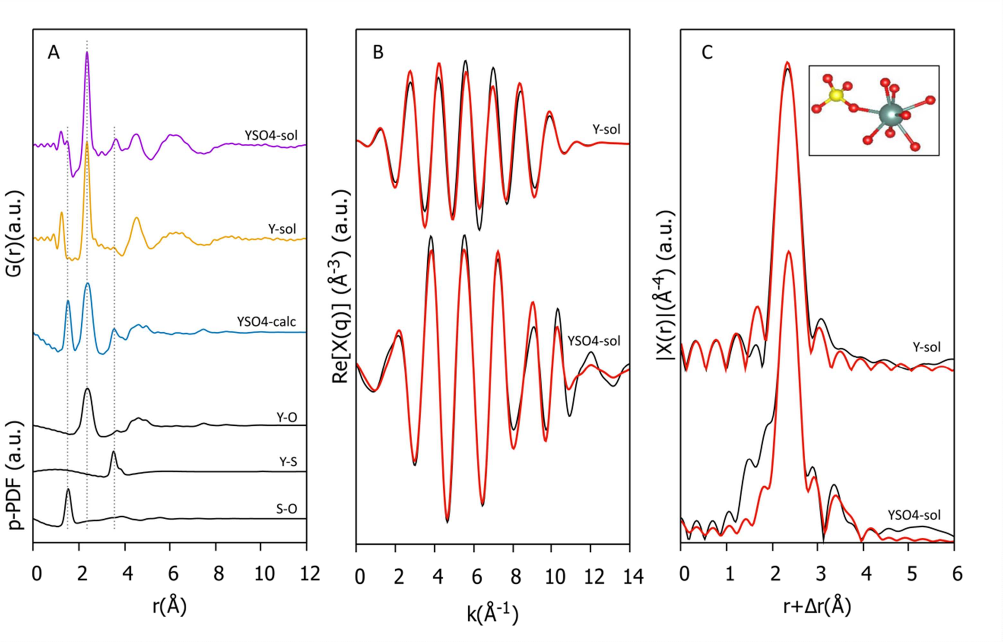

Figure 2.5 (A) Top: Experimental PDFs of YSO4-sol and Y-sol samples. Bottom: Simulated (AIMD) PDF (YSO4-calc) and its partial PDFs. (B) Fourier-filtered signal f(1.8 to 4.2 Å) and (C) EXAFS FT amplitude functions EXAFS data. Black lines: experimental; red lines: fits. Simulated (AIMD) PDF and partial PDFs have been multiplied for visualization purposes: YSO4-cal (x3), Y-S (x5) and Y-O and S-O (x2). Dashed lines indicate the position of the Y-O, Y-S and S-O bonds in YSO4-sol sample.

The experimental PDF for solution with the aqueous YSO_4^+ specie (YSO4-sol) presented a peak at 2.37 Å, which corresponds to the Y-O interatomic distances to oxygen to the first shell (Figure 2.5). A small and sharp peak at 1.45 Å corresponds to the S-O interatomic distance in sulfate. Finally, another smaller peak at 3.7 Å, was concomitant to the analyses of the AIMD trajectories that showed a distance of 3.6 Å between Y and S. Fits of the EXAFS spectra of the YSO_4^+ aqueous solution were performed using atomistic models from the AIMD simulations as initial structural models for the generation of the scattering paths. The best fit yielded an average Y−O distance of 2.38 ± 0.01 Å and

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[3] *This part of the thesis is base don the article Lozano et al., 2019b, ES&T, doi: 10.1021/acs.est.9b01795*

the coordination number (CN) of 7.9±0.9, close to 8, the expected for HREEs. The second shell observed in the FT was fitted with a Y-S distance of 3.5 ± 0.04 Å, similar to that observed in the PDF of the same sample, with a CN =1. Thus, the structure of the aqueous YSO_4^+ forms a monodentate inner-sphere complex (one shared oxygen) between sulfur and yttrium.

2.3.2 Local order of yttrium adsorbed onto basaluminite

All the EXAFS spectra of solid references (B-YSO4-ads, B-Y-ads, B-Y-cop and A-Y-ads) are indistinguishable and differ from the aqueous Y-sol and YSO4-sol spectra in that a slight oscillation becomes visible at 5-6 $Å^{-1}$. In the B-YSO4-ads (YSO_4^+ sorbed onto basaluminite) the dominant Y species in solution is the YSO_4^+ complex (Figure 2.6). However, in B-Y-ads (Y^{3+} sorbed onto basaluminite), B-Ycop (Y^{3+} coprecipitated in basaluminite) and A-Yads (Y^{3+} sorbed onto nanoboehmite), the dominant Y species is Y^{3+}. Since the common feature in these three samples is the presence of an Al adsorbent, and this feature agrees with that in the B-YSO4-ads EXAFS spectrum, we hypothesize that the higher frequency observed at 5-6 $Å^{-1}$ (arrow in Figure 2.6) may be related to the presence of an Al backscatterer, rather than to a signal from a close sulfate group. Both Al and S are light atoms with similar atomic numbers (Z = 13 and 16, respectively), which makes their backscattering functions difficult to distinguish via fitting of the EXAFS signal. These observations lead us to assume that the EXAFS measurements have poor sensitivity to the presence of Y-S bonds in this system. However, a contribution from a sulfate shell for the two first samples cannot be ruled out.

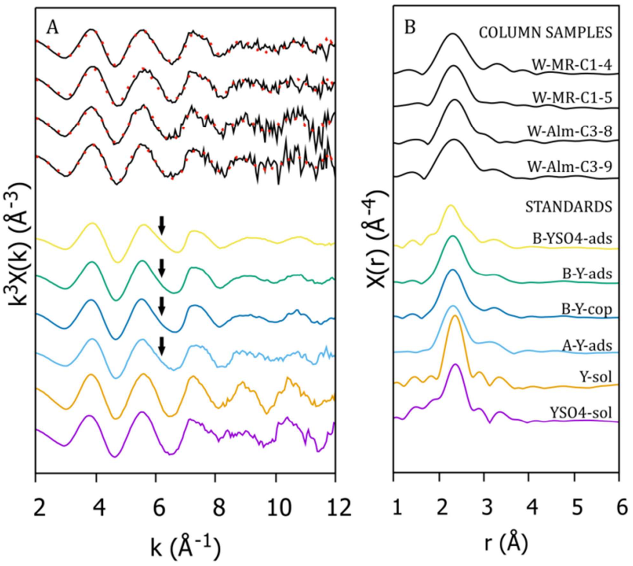

Figure 2.6. k^3-weighted EXAFS (A) and FT amplitude functions (B) for four waste samples from column treatments W-MR-C1-3, W-MR-C1-4, W-Alm-C3-8, and W-Alm-C3-9 (upper part) and solid standards: B-YSO_4-ads, B-Y-ads, B-Ycop; and aqueous solution standards: Y-sol and YSO4-sol (bottom part). The dashed lines in the EXAFS signals of the column samples represent LCF with B-YOS-ads and YSO4-sol.

Three different atomistic models were used to fit the EXAFS of a basaluminite sample with YSO_4^+ sorbed into its surface (B-YSO4-ads): (A) a monodentate surface complex, (B) a bidentate mononuclear surface complex and (C) a bidentate binuclear surface complex. The monodentate inner sphere complex was one of the best EXAFS fit, where the fit was performed assuming S and Al coordination numbers equal to 1 and 2, respectively. The fit yielded a first coordination shell with a Y-O distance range between 2.32 and 2.47 ± 0.02 Å with a fixed coordination number of 8. The second best fit, was the bidentate binuclear inner-sphere. The first shell was fitted with a coordination number of 10 ± 1.31 and a distance of 2.33 Å. The second shell was fitted with a S path yielding a Y-S distance of 3.34 Å with a fix coordination number of N = 1, similar to that for the monodentate hypothesis, and with an Al path with a fixed coordination number of N = 2 giving a distance a bit longer, 3.92 Å.

Table 2.1 Results of the EXAFS fits for B-YSO4 reference. Model 1: monodentate inner sphere. Model 2: bidentate mononuclear inner sphere. Model 3: bidentate binuclear inner sphere. Var.: independent variables. The best model is indicated with a star (*). The error is expressed in the parentheses after the last digit

Model	Neighbor	path	N	σ^2	ΔE_0	R	Var.	χ_ν^2
1*	1st shell	Y-O$_1$	6_{fix}	0.007(1)	-3(2)	2.32(1)	9	338
		Y-O$_2$	2_{fix}	0.004(8)	-3(2)	2.47(2)		
	2nd shell	Y-S	1_{fix}	0.008(5)	-3(2)	3.33(4)		
		Y-Al	2_{fix}	0.012(5)	-3(2)	3.52(5)		
2	1st shell	Y-O	10 (1)	0.012(2)	-6(2)	2.33 (1)	8	402
	2nd shell	Y-S	1_{fix}	0.009(5)	-6(2)	3.88 (5)		
		Y-Al	1_{fix}	0.006(3)	-6(2)	3.42 (3)		
3	1st shell	Y-O	10(1)	0.013(1)	-4(1)	2.33(1)	8	334
	2nd shell	Y-S	1_{fix}	0.008(3)	-4(1)	3.34(3)		
		Y-Al	2_{fix}	0.011(5)	-4(1)	3.92(4)		

2.4 REE distribution in the column experiment[4]

The results of the mobility of REE in a column experiment simulating a passive remediation system are shown in Figure 2.7. Only Sc, La and Y were compared due to their different sorption behavior in the column experiment results. Essentially, for a given time the pH increased with depth, and for a given depth the column was progressively invaded by more acidic water (Figure 2.7 A). For each time, Fe and Al concentrations decreased with depth to detection level suggesting the precipitation of schwertmannite and basaluminite (Figure 2.7 B-C). However, Al showed a peak of concentration higher than the input AMD. This was already observed in previous column experiments, and attributed to the re-dissolution of basaluminite by the percolating AMD once the calcite reagent was exhausted (Rötting et al., 2008b). Practically no Al and Fe were detected at the end of the column in the four sampling events.

The concentration of the three selected REE showed a similar distribution pattern (Figure 2.7 D-F) in depth. As described for Al, the concentration decreased with depth, also showing a peak of concentration higher than the input AMD. This distribution suggests a close association of REE to basaluminite, as already observed for Y and lanthanides in previous experiments (Ayora et al., 2016). In subsequent samplings, the peak concentration decreased to the value of the inflow AMD value. Scandium, however, showed a slightly different behavior. For the same sampling event (28 days), the Sc peak was observed to occur upstream with respect to those of La and Y, and for the same depth (10 cm), the Sc peak took longer time to disappear. As for Fe and Al, almost no REE concentration was detected at the end of the column during the experiment.

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[4] *This part of the thesis is based on the article Sorption of rare earth elements on schwertmannite and their mobility in acid mine drainage treatments. App. Geochem. Submitted*

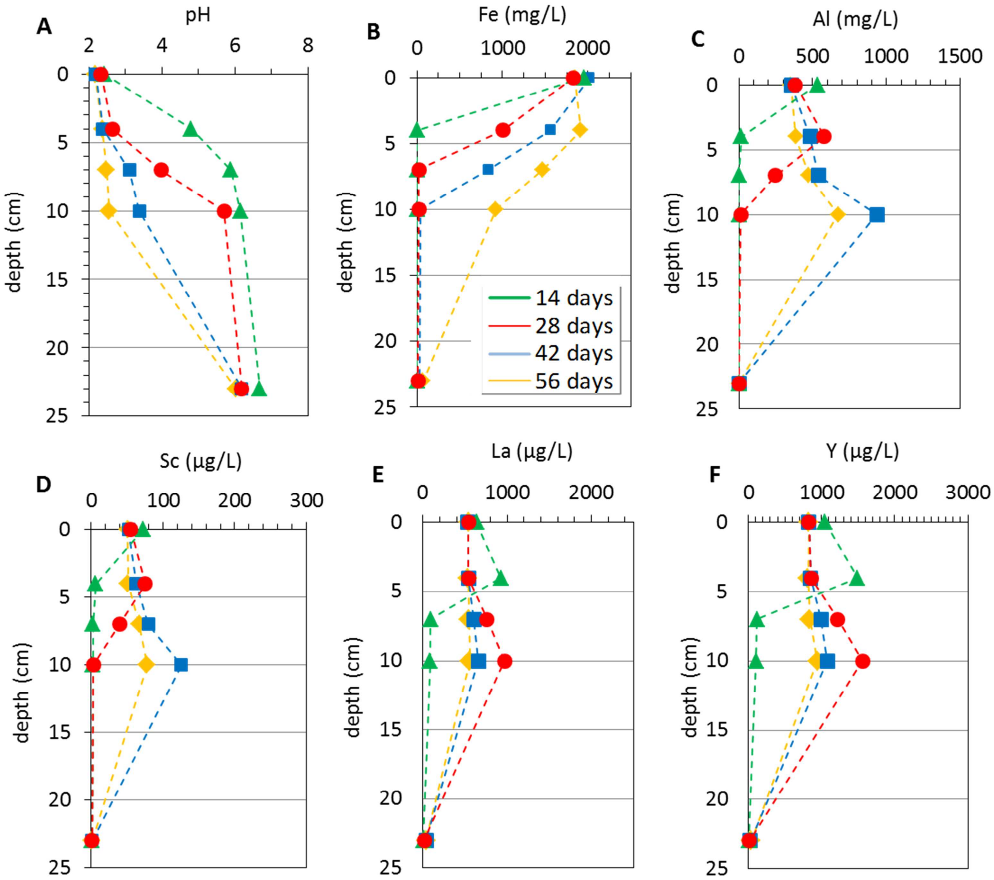

Figure 2.7 Depth profiles of pore water and solid composition at four different stages of column operation: (A) pH evolution; (B, C) Fe and Al concentrations in pore water; (D, E, F) mineral distributions; (G, H, I) concentrations of selected REE in pore water.

Once the column was stopped after 58 days of functioning, and the solid residue was dried and sliced for analysis, sequential extractions were carried out. As evidenced in Figure 2.8 D-E, a minor proportion of Sc and the rest of the REE was found in the water-soluble step I, most likely linked to gypsum (Lin et al., 2019). However, most REE were found in steps II and III, which are representative of schwertmannite and basaluminite. However, some differences are evident in the depth distribution of Sc and the rest of the REE. Yttrium (and lanthanides) match the Al distribution along the column depth (Figure 2.8 E), indicating that they are attached to basaluminite. However, up to 25% Sc was located in the first 6 cm of the column, matching the Fe distribution and suggesting a link to schwertmannite.

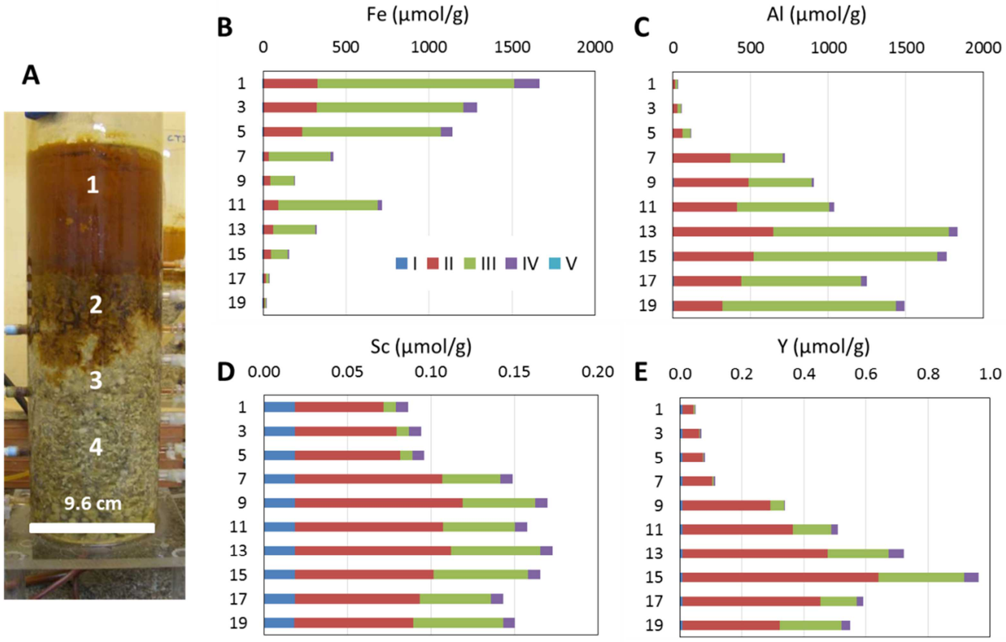

Figure 2.8 (A) View of the column after 28 days of the experiment: 1= supernatant AMD; 2= schwertmannite zone; 3= basaluminite zone 4= calcite zone. (B-E) Distribution of Fe, Al, Sc and Y concentration in the solid residue. The numbers on the vertical axes indicate the depth (cm) of the center of each slice of the column. The colors indicate the different steps of sequential extraction of the following phases: I) the water-soluble fraction; II) calcite and basaluminite, III) low crystalline Fe(III)-oxyhydroxides and remaining basaluminite, IV) crystalline Fe(III)-oxides, and V) the residual fraction.

2.5 REE behavior in the mixing streams[5]

2.5.1 Description of the field sites and sampling

2.5.1.1 Odiel river sites

The Odiel River is a 122 km long and has a catchment area of 2300 km^2, from the Aracena Mountains in the North of Huelva province to Huelva estuary in the South, a region in the Southwest of Spain. In this area, about one hundred of ancient mines and wastes generating AMD have been detected in the Odiel watershed (Sánchez-España et al., 2005a; Nieto et al., 2013).

Water samples were collected from the five water discharges (CN, SP, ES, PO and AG) and from the Odiel river prior the discharges and more than 100 m downstream, when water mixing was apparently complete (Figure 2.9).

The field sampling was completed with several localities from the same area. Thus, water samples and precipitates from Dehesa Boyal and Torerera mine correspond to the mixing of a small acidic stream with less than 2 L/s (DB, TO) with a higher flow of near neutral water (DB-neu and TO-neu, respectively). The Rio Tinto (RT) locality corresponds to the reverse situation. Upstream the village of Niebla, a small neutral stream of less than 5 L/s discharged into the Rio Tinto main stream (1 m^3/s).

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[5] *This part of the thesis is based on the article Modeling the behavior of the rare earth elements in acid drainages: achievements and limitations.*

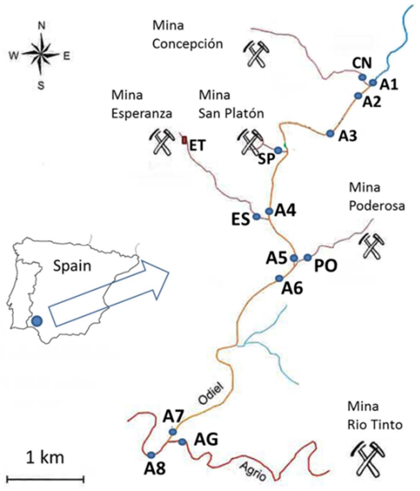


Figure 2.9 Stretch of the Odiel river and acidic tributaries with the sampling points.

Finally, a full scale passive remediation system was working in 2007-8 at Mina Esperanza site (ET in Figure 2.9). The system consisted in a limestone sand filter intercalated in the acid water flow. A full description of the water and solid waste chemistry and mineralogy is in Caraballo et al. (2011a,b). Three solid samples of white precipitates were collected on different days at the outflow channel of treatment plant.

2.5.1.2 Arroyo del Val site

The information corresponding to Arroyo del Val area is mainly extracted from Auqué et al. (1993) and Gimeno (1999). The Arroyo del Val is located between Luesma and Fombuena villages, about 70 km SW Zaragoza, Spain. The section studied of the Arroyo del Val stream is about 3 km long, it carries more than 10 L/s after rain events, and less than 1 L/s during summer. The stream is excavated in a monotonous series of dark brown to black shale of Silurian age, that crop out in the drainage basin. The black shale contains dispersed abundant sulfides, mainly pyrite, which generates an ubiquitous acid rock drainage (ARD) after weathering. Differently from most of the Odiel sites, the Arroyo del Val is an acidic stream that receives several neutral tributaries of near neutral pH (Figure 2.10). The mixing of waters yields iron and especially aluminum rich flocculates that sediment at and downstream the confluences. Water (labeled with W) and solid (labeled with C) samples were collected in three different campaigns, and only those pairs of coexisting water and precipitates were selected: 1991 (W5-CV1), 1994 (W9-C9; W12-C12) and 1996 (Wexp-Cexp).

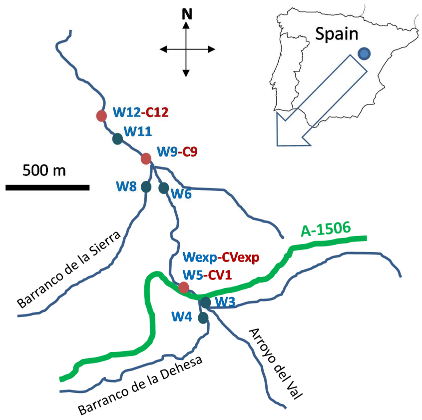


Figure 2.10 Sketch of the Arroyo del Val system. Each letter corresponds to different samples (W= water; C= precipitates).

2.5.2 Chemical evolution after mixing points

The values of the chemical composition of the aqueous phase in each sampling point of the Odiel river stretch is compared with those resulting from the conservative mixing of the river and any acidic discharge (Figure 2.11). Although some amount of SO_4 was removed from water due to Fe and Al oxy-hydrosulfate precipitates, its high concentration made it a quasi-conservative solute (Figure 2.11 A). On the contrary, Fe and As are clearly not conservative at both acidic and neutral pH (Figure 2.11 B), indicating their removal by the precipitation of schwertmannite (Carlson et al 2002; Fukushi et al., 2004). Al and Cu showed an intermediate behavior (Figure 2.11 C). They are partially removed by precipitates in the upper part of the river, where pH remained always above 6.5, and they behaved conservatively at low pH when the Agrio acidic discharge caused a final pH of the river lower than 3.5. Similar behavior was experienced by REE. They were complete removed by the precipitates at pH higher than 6.5 and they behaved conservatively at pH below 3.5. This observation is consistent with the behavior described by previous authors (Verplank et al., 2004; Gammons et al., 2005a, b; Ferreira-da-Silva et al., 2009), and suggests that, rather than schwertmannite, basaluminite is responsible for scavenging REE from water.

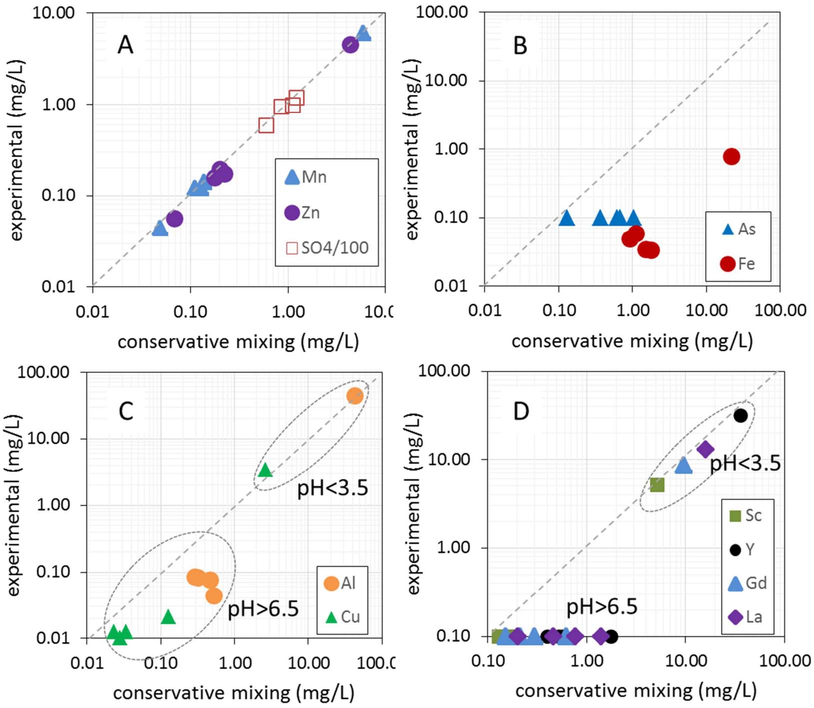


Figure 2.11 Comparative between experimental and conservative concentration of selected elements in samples from the Odiel river after receiving acid discharges.

2.5.3 Precipitates

Reddish-ochreous and whitish precipitates or mixtures were taken from the two sampled localities. They are formed by aggregates of spherical particles of less than 0.1 µm forming aggregates of larger size. In most of the reddish precipitates, the pink-cushion texture typical of schwertmannite can be distinguished, whereas only aggregates of spheres were observed in the whitish precipitates. Schwertmannite was only clearly identified in AG, DB and TO reddish precipitates floating in the water, and basaluminite in whitish precipitates from AG, TO, DB and ET. In the rest of localities, the existence of basaluminite was deduced from the chemical analyses.

The whitish precipitates from AG, DB, TO and ET showed variable but minor Fe concentrations and Al/S ratios ranging from 4.32 to 6.26, higher than the theoretical basaluminite formula,

$Al_4SO_4(OH)_{10}\cdot 5H_2O$, probably due to mixtures with Al hydroxides and/or its partial transformation into low crystalline bohemite and the release of SO_4 (Lozano et al., 2018). The precipitates from PO and RT show high contents in both Al and Fe, and S concentrations below 3 wt%, and (Fe+Al)/S ratios from 7.5 to 12, far above what is expected for schwertmannite and basaluminite. These samples are coincident with pH values of the mixtures above 6, and they are interpreted as mixtures of these minerals with Al and Fe hydroxides (Bigham et al., 1996; Nordstrom and Alpers, 1999). Silica was always present in basaluminite analyses with Al/Si molar ratios between 21 and 180, with the higher ratio in DB, 500 m away from the water mixing. Similar distribution of Al/Si ratios are reported by Caraballo et al. (2019).

The precipitates from Arroyo del Val were formed by Al (16 to 18 wt.%), Fe (25 to 29 wt.%) and S (6 to 11%), and minor amounts of Si (1 to 6 wt.%) (Gimeno, 1999). Moreover, microprobe analyses of the whitish amorphous phase always reveal the presence of S with ((Al+Fe)/S) ratios close to 4, which indicates that schwertmannite and basaluminite could be major phases.

The results of the REE patterns from solids recovered in different field sites are plotted in Figure 2.12. The REE patterns of the original acid water are also plotted as a reference. As can be observed, the main trends of REE distribution of the water are transferred to the solid phase. Thus, all the NASC-normalized REE patterns of waters and precipitates show a typical convex curvature indicating enrichment in MREE with respect to LREE and HREE, which has been also described for other acid drainages (Ferreira-da-Silva et al., 2009; Perez-Lopez et al., 2010; Sahoo et al., 2012). All the water samples from the Odiel-Tinto basins show a characteristic Eu negative anomaly, although this anomaly varies from being acute in AG and ET (Figure 2.12 A, C) to less acute in other points of the Odiel -Tinto area. The Eu anomaly is absent in the samples from the Arroyo del Val site (Figure 2.12 D-F). The reason for this different pattern seems, therefore, related to the different original rocks and mineralization types of both regions, felsic volcanics in Odiel-Tinto and sedimentary black shales in Arroyo del Val. As exception, some precipitates from Arroyo del Val show a negative anomaly in Gd that is not observed in the aqueous phase (and neither confirmed by the model).

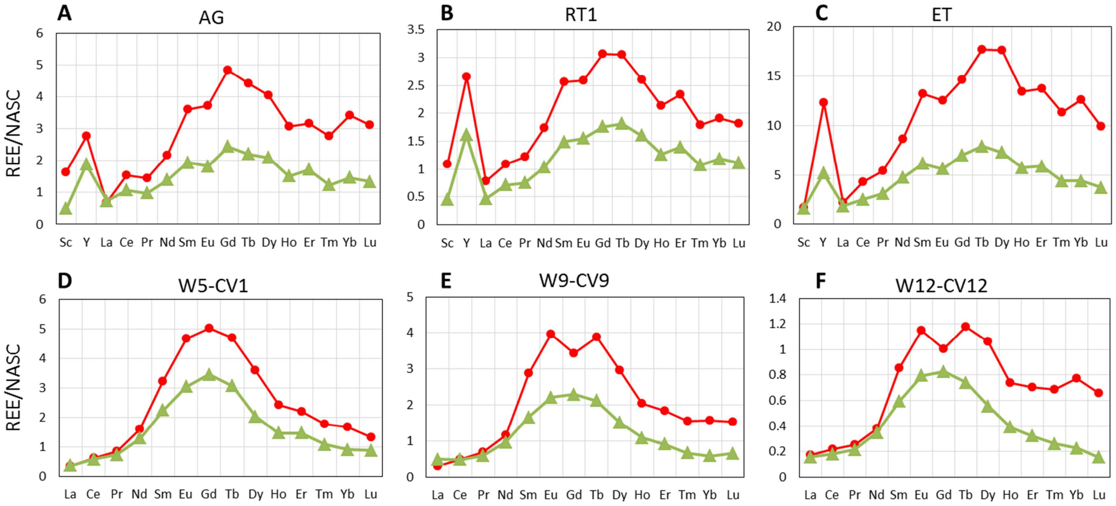


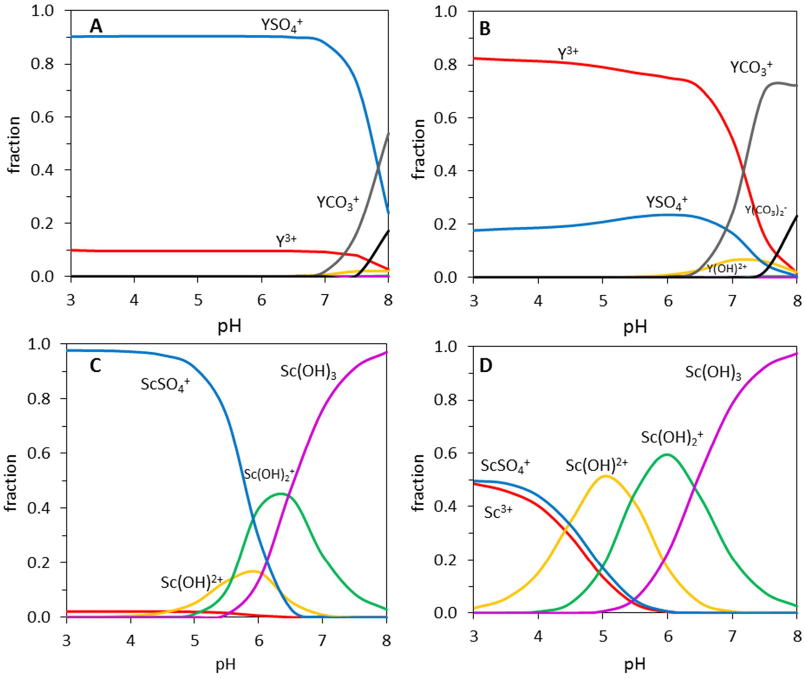
Figure 2.12 REE patterns of precipitates (red circles) and of the parent AMD (green triangles). All the concentrations normalized to North American Shale Composite (NASC). (A, B, C) Samples from Odiel-Tinto site, (D, E, F) Samples from Arroyo del Val site.

3 Discussion

3.1 Sorption model[6]

3.1.1 REE aqueous speciation

Sulfate is ubiquitous in AMD environments with concentrations that can range from mg/L to g/L. Moreover, sulfate strongly complexes with aqueous REE (Gimeno Serrano et al., 2000), forming the aqueous $REESO_4^+$ specie (MSO_4^+ hereinafter), and thus becoming the major aqueous specie in solution (Figure 3.1 A). Sc behaves some different since besides $ScSO_4^+$, the aqueous speciation showed a higher stability of the hydrolysis species $Sc(OH)^{2+}$ in the experiments with lower sulfate concentration Figure 3.1 C,D). Thus, since sorption of REE increases with higher sulfate in solution, is expected that the sorption of MSO_4^+ occurs onto the basaluminite surface, with probably some exception to Sc sorption.



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[6] *This part of the thesis is based on the articles Lozano et al., 2019a. Geochim. Cosmochim. Acta 258, 50-62, and Lozano et al., 2019c. App. Geochem. Submitted.*

Figure 3.1 Aqueous species distribution of Y and Sc with pH for a solution with 20 mM (A, C) and 0.5 mM (B, D) of sulfate at 25 °C and atmospheric pCO2.

3.1.2 Description of sorption model

A non-electrostatic model (NEM) is a type of Surface Complexation Model (SCM) in which the electrostatic term is ruled out when the chemical interaction of the cation adsorption is stronger than electrostatic forces (Davis and Kent, 1990). In particular, several works have modeled the sorption experimental data of some REE with NEM, discarding the electrostatic term, such as Marmier et al. (1999) to describe the sorption of lanthanum in hematite; Tertre et al. (2008) to describe REE adsorption on basaltic rock, or Rabung et al. (2000) and Quinn et al., (2006a,b) to describe Y and lanthanides sorption in amorphous iron hydroxides. The SCM models are characteristic in part due to its adjustable parameters. Such as equilibrium constants, total number of reactive sites, and capacitance density. In the case of basaluminite and schwertmannite, its metaestable character of the mineral precluded the full determination of its surface properties and thus, a non-electrostatic model was used.

Owing to the predominance of aqueous sulfate complexes in the solutions (Figure 3.1), the sorption experiments were modeled by the reaction of the aqueous sulfate complex MSO_4^+ with the free surface sites of the two minerals studied. This assumption is consistent with the observation of higher adsorption in the experiments with the SO_4-rich solutions (20 mM) with basaluminite. In the case of Sc, in addition to $ScSO_4^+$, the aqueous speciation showed a higher stability of the hydrolysis species $Sc(OH)^{2+}$ in the experiments with lower sulfate concentration and the sorption of this aqueous species was also considered. Although experiments were conducted at room conditions, carbonate complexation has not been considered experimentally since the proportion of carbonate species is very low at the experimental pH range (Figure 3.1).

The sorption reaction is proposed as the exchange of the M^{z+} aqueous complex (M^{z+} accounting for MSO_4^+ and $Sc(OH)^{2+}$) with n protons from n surface sites represented by XOH:

$$M^{z+} + nXOH = (XO)_nM^{z-n} + nH^+ \qquad K_M \qquad \textit{Eq. 3.1}$$

The equilibrium constant K_M of the reaction for each REE (M) would be:

$$K_M = \frac{\{(XO)_nM^{z-n}\} \cdot a_{H^+}^n}{a_{M^{z+}}\{XOH\}^n} \qquad \textit{Eq. 3.2}$$

where a_{Mz+} and a_{H+} are the activities of the aqueous complex and proton, respectively; and $\{(XO)_nM^{z-n}\}$ and {XOH} account for the mole fraction of the sorbed species ($[(XO)_nM^{z-n}]/[T_{XOH}$) and the free surface sites ($[XOH]/T_{XOH}$), respectively.

From the total surface site concentration previously calculated for basaluminite and schwertmannite, the concentration of free surface sites was calculated as:

$$[XOH] = TXOH - \sum n\,[(XO)nMz - n] \qquad \textit{Eq. 3.3}$$

The value of the equilibrium constant K_M for each element was obtained with data from the experiment with 20 mM SO_4, except for the case of the species $Sc(OH)^{2+}$, which was obtained from the experiments with 0.5 mM SO_4 basaluminite and 2 mM SO_4 for schwertmannite.

Thus, replacing the molar fraction by their values, taking logarithms of Eq. (4.2) and rearranging the order we obtain a linear expression (Eq.4.4):

$$\log\frac{[(XO)_nM^{z-n}]}{a_{M^{z+}}}\log = \log K_M + n\,pH + n\log[XOH] - (n-1)\log T_{XOH} \qquad \textit{Eq. 3.4}$$

For low occupancy of surface sites, [XOH] and T_{XOH} are practically coincident and Eq. 4.4 can be approximated as:

$$\log\frac{[(XO)_n M^{z-n}]}{a_{M^{z+}}} = \log K_M + n\,pH + \log T_{XOH} \qquad \textit{Eq. 3.5}$$

Therefore, the equilibrium constants determined here ($K_M \cdot T_{XOH}$) are those referred to as the K_3 according to the model 3 proposed by Wang and Giammar (2013).

By plotting the experimental data of the set of sorption experiments performed with 20 mM aqueous sulfate on basaluminite and schwertmannite minerals, linear correlations were obtained according to Eq. 4.5 for Y and lanthanide series (Figure 3.2).

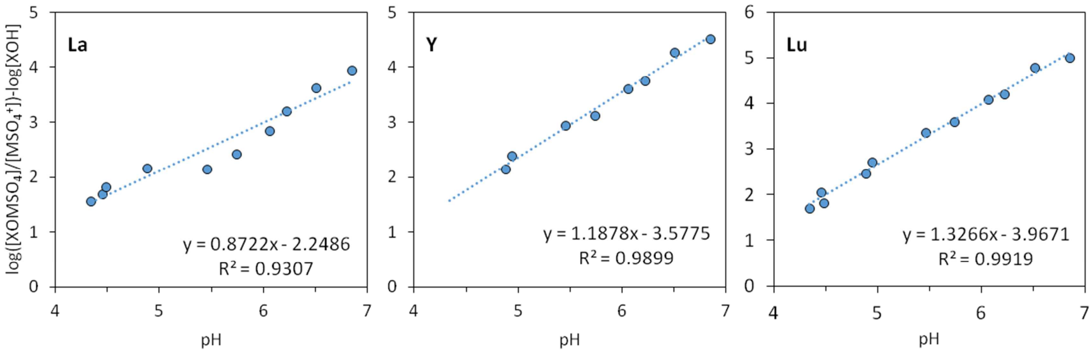

Figure 3.2 Regressions obtained from measured pH values and calculated activities from the final concentrations of experimental data following the Eq. 4.5 for the experimental set of 20 mM SO_4 for basaluminite Regressions for Y, La and Lu, from basaluminite, (A,B,C).

The slope of the regressions obtained from experiments with 20 mM SO_4 was close to 1 for yttrium and lanthanides in basaluminite mineral (Figure 3.2) and varied from 1.5 to 2 in schwertmannite. A slope close to 1 suggests the exchange of the MSO_4^+ with one surface proton and the formation of a monodentate surface complex, as indicated by the Eq. 4.1 (Rabung et al., 1998; Rabung et al., 2000). The results of EXAFS fits of a sample of basaluminite with sorbed YSO_4^+ on its surface indicated the formation of a monodentate inner sphere (Table 2.1) and are consistent with the model description of REE sorption onto basaluminite. Similar EXAFS results were obtained by Rabung et al. (2006), where Gd and Lu formed inner sphere surface complexes onto γ-Al_2O_3. Lu, which is considered a HREE such as Y, was shown to form a monodentate surface complex with a first shell of 7 atoms and a Lu-O distance of 2.28 Å.

Likewise, the values close to 2 from sorption experiments with schwertmannite were interpreted as the exchange with two surface protons and thus, the formation of a bidentate surface. Similar bidentate complexes were obtained by EXAFS fitting analysis of Lu sorbed onto ferrihydrite and Eu sorbed onto hematite (Dardenne et al., 2001; Estes et al., 2013). However, due to the variation, a small proportion of monodentate complexes could also be present.

Unlike Y and the lanthanides, the linear regression for $ScSO_4^+$ data from the 20 mM SO_4 experiments for the two minerals resulted in a slope close to 2. Similar results were observed for $Sc(OH)^{2+}$ with a slope of 1.90 from the experiment with 0.5 mM SO_4 with basaluminite (Figure 3.3), and with a slope of 1.49 from the experiment with 2 mM SO_4 with schwertmannite. Again, in both cases, a slope of 2 suggests the formation of bidentate surface complexes.

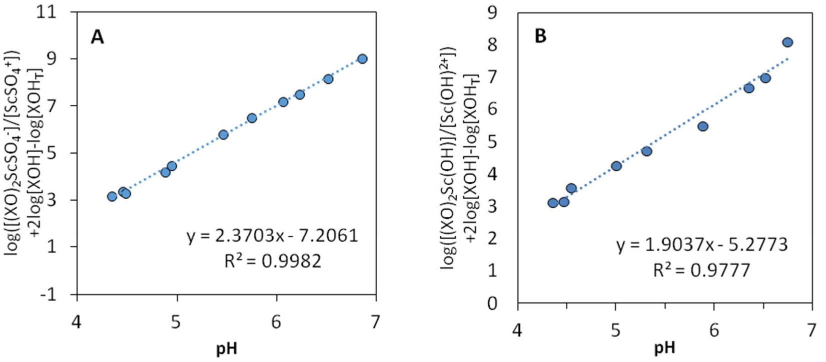

Figure 3.3 Regressions obtained from experimental data from Sc element plotted according the linearized equations (n = 2) for $ScSO_4^+$ (A) and for $Sc(OH)^{2+}$ (B).

To obtain surface sorption equilibrium constants, the regression slopes from experimental data sets of 20 mM SO_4 were forced to 1 for yttrium and lanthanides and to 2 for Sc, for the experiments performed with basaluminite; and forced to 2 for all REE for experiments carried out with schwertmannite, respectively using Gnuplot v. 5.2.7 software (Williams and Kelley, 2019). The calculated log K_M values and the regression errors for surface complexation reactions for all REE are listed in Table 3.1. The log K_M values for both minerals increase from La to Lu in both minerals, indicating the higher HREE affinity over LREE.

Table 3.1 Equilibrium constants for the formation of surface complexes (K_M of Eq. (3)) obtained by fitting the experimental values of the two set of sorption experiments with 20 mM SO_4 with basaluminite and schwertmannite solids, respectively. Concentration of the surface species calculated as their molar fractions (K_M is the K_3 value of Wang and Giammar (2013).

Mineral	Basaluminite			Schwertmannite		
Element	Surface Complex	Log K_M	Error	Surface complex	Log K_M	Error
Sc	$(XO)_2ScSO_4^-$	-5.19	0.08	$(XO)_2ScSO_4^-$	-5.27	0.07
	$(XO)_2Sc(OH)$	-5.81	0.09	$(XO)_2ScOH$	-3.4	0.08
Y	$XOYSO_4$	-2.48	0.06	$(XO)_2YSO4^-$	-7.62	0.04
La	$XOLaSO_4$	-2.95	0.08	$(XO)_2LaSO4^-$	-7.96	0.15
Ce	$XOCeSO_4$	-2.81	0.07	$(XO)_2CeSO4^-$	-7.6	0.10
Pr	$XOPrSO_4$	-2.69	0.05	$(XO)_2PrSO4^-$	-7.52	0.13
Nd	$XONdSO_4$	-2.60	0.03	$(XO)_2NdSO4^-$	-7.44	0.09
Sm	$XOSmSO_4$	-2.48	0.05	$(XO)_2SmSO4^-$	-7.27	0.08
Eu	$XOEuSO_4$	-2.50	0.05	$(XO)_2EuSO4^-$	-7.41	0.09
Gd	$XOGdSO_4$	-2.50	0.04	$(XO)_2GdSO4^-$	-7.51	0.05
Tb	$XOTbSO_4$	-2.48	0.06	$(XO)_2TbSO4^-$	-7.42	0.06
Dy	$XODySO_4$	-2.37	0.06	$(XO)_2DySO4^-$	-7.27	0.03
Ho	$XOHoSO_4$	-2.40	0.05	$(XO)_2HoSO4^-$	-7.38	0.06
Er	$XOErSO_4$	-2.40	0.11	$(XO)_2ErSO4^-$	-7.39	0.05
Tm	$XOTmSO_4$	-2.27	0.08	$(XO)_2TmSO4^-$	-7.17	0.08
Yb	$XOYbSO_4$	-2.13	0.08	$(XO)_2YbSO4^-$	-7.26	0.04
Lu	$XOLuSO_4$	-2.19	0.09	$(XO)_2LuSO4^-$	-7.13	0.09

3.1.3 Model validation

Log K_M values from experimental data of sorption conducted at high sulfate concentration were tested with the results from sorption experiments with lower sulfate content: 0.5 mM (in experiments with basaluminite) and 2 mM SO_4 (in experiments with schwertmannite). The sorption fraction for each REE was calculated with the PHREEQC software, taking into account the experimental conditions (temperature of 25°C and a pCO_2 of 3.5) and the surface properties of the minerals calculated previously.

Only in basaluminite experimental results, at higher pH values than 6.5 a mismatch between the modeled sorbed fractions and the experimental ones (symbols) for the experiment with the lower sulfate content is attributed to the presence of dissolved carbonate species. Thus, MCO_3^+ species form and take part in the sorption process. To show the possible role of carbonate complexes at pH higher than 6.5 and low sulfate concentration, the sorption of MCO_3^+ complexes has been included in the model. The equilibrium constants for the MCO_3^+ sorption reactions have been recalculated from those reported by Quinn et al. (2006b) for goethite. Including carbonate complexation, the model predicts sorption at near neutral pH when lower sulfate is present in solution, supporting the role of carbonate complexation at such particular conditions (Figure 3.4 A,B).

As expected, the model reproduces well the sorption edges in the experiments with 20 mM SO_4 (Figure 3.4 B,D) with occasional predictions outside the experimental error. Although worse, the model for the experiment with lower sulfate concentration is also acceptable, and the predicted values in general fit the analyses within the experimental error (Figure 3.4 A,C). The good fit between the predicted and measured Sc values confirms a good model prediction for the formation of bidentate surface complexes with $ScSO_4^+$ and $ScOH^{2+}$ with the surfaces of the two minerals.

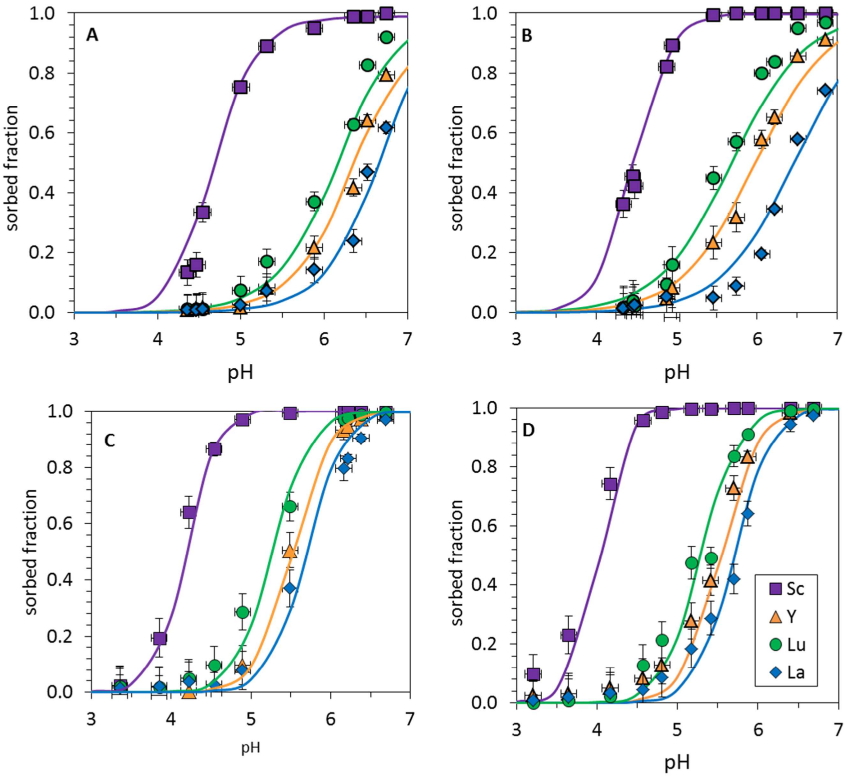

Figure 3.4 Experimental (symbols) and calculated fractions (lines) of the sorption curves for Sc, Y, La and Lu for the experiments (A) with 0.5 mM SO_4 in basaluminite solids and (B) 2 mM SO_4 in schwertmannite. Calculations at 25°C and atmospheric CO_2 pressure.

Finally, the model was also validated with data sets of new sorption experiments varying the solid:liquid ratios and keeping constant the concentration of 20 mM dissolved sulfate. As expected, the model predicts lower adsorption for the lower 0.25 g/L basaluminite suspensions (Figure 3.5A). In the case of schwertmannite, despite a slight overprediction at higher pH values for the 0.25 g/L solid:liquid ratio, the sorbed fractions for 2 g/L suspensions were successfully predicted by the model within the experimental errors (Figure 3.5 B).

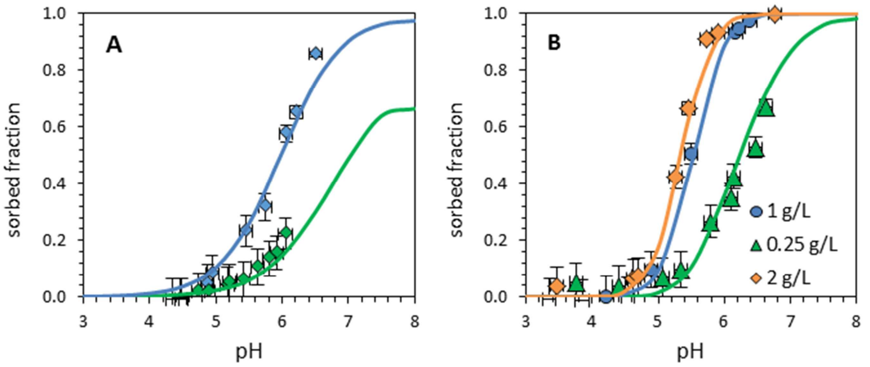

Figure 3.5 Comparison between experimental data (symbols) and calculated fraction (lines of the sorption edge curves for sorbed Y in 20mM SO4 solutions with (A) basaluminite and (B) schwertmannite, at different solid liquid ratios. Calculations at 25°C and pCO$_2$ of 3.5.

3.2 REE behavior in passive remediation systems

The surface complexation model validated with experimental data let us to predict the behavior of REE in laboratory-scale columns of passive remediation systems and also to explain the REE partition between solids and acidic waters when mixing with circumneutral streams in the field.

The prediction of the mobility of REE in pore water of a column system was performed with a reactive transport model accounting the calcite dissolution according to the kinetic low described by Plummer et al., 1979. The results of the 1D reactive transport model (lines) were used to interpret the experimental data (symbols) (Figure 3.6). For a given time the pH increased with depth, and for a given depth the column was progressively invaded by more acidic water. A schwertmannite front appeared first, at lower pH values (pH 2.5), followed by a basaluminite front (pH 3.8), and both fronts advanced with time (Figure 3.6 D,E). This solid phase distribution along the column is identical to that observed in other column experiments and field scale treatments (Rötting et al., 2008a; Rötting et al., 2008b; Caraballo et al., 2009; Caraballo et al., 2011b). The calculations confirm that when calcite started to be exhausted from the top of the column downwards (Figure 3.6 F), the acid water, although did not affect to the precipitated schwertmannite, it dissolved the basaluminite and the Al concentration in the pore water increased above the inflow concentration (Figure 3.6 C).

According to Figure 3.4, Sc can sorb from pH 3-3.5, so this element could also sorb on schwertmannite precipitates. Unlikely, lanthanides and Y start to sorb at least one pH unit higher and sorption of these elements was only expected in basaluminite. These differences are reflected in the log K$_M$ values, which were similar between La and Y but clearly differed with respect to Sc values. Thus, the similar La and Y distribution in pore water in contrast to the different behavior of Sc with respect to La and Y was evidenced in both the measured and calculated pore water concentrations (Figure 3.6 G-I).

For each time span, the different mobility between Sc, Y and lanthanides due to sorption processes depends on the pH at a given depth, which is in turn related to the schwertmannite and basaluminite precipitation. Thus, for a specific time and a given depth, the pH varies, varying the sorbed ratio of each element. At longer times due to the progressive calcite exhausting and thus the progress of the acidic water with depth, a partial desorption of lanthanides and yttrium with sorption of Sc could occur between pH 3 and 6. Thus, the similar La and Y distribution in pore water, in contrast to the different behavior of Sc with respect to La and Y, was evidenced in both the measured and calculated pore water concentrations (Figure 3.6 G-I).

The calculated solid phase distribution at the end of the column life (Figure 3.6 D-E, 56 days) was also consistent with that deduced from sequential extraction analyses (Figure 2.8). The calculated pH value in the lowermost 10 cm ranged from 3.8 to 6, indicating that La, Y and Sc could remain sorbed on basaluminite, in accordance with sequential extraction analyses and with the absence of REE in the column outflow. However, the calculated pH value in the uppermost 10 cm was 2.5, buffered by schwertmannite precipitation. At such pH, basaluminite was dissolved releasing to the pore water all the REE sorbed in earlier stages of the column. Also Sc, if partially sorbed on schwertmannite would be desorbed (Figure 3.4). Therefore, the Sc analyzed in the upper 10 cm of solid residue indicates that desorption was not entirely reversible. Indeed, desorption has also been reported to be a very slow process in experiments of Yb sorption on hematite and alumina (Marmier et al., 1997).

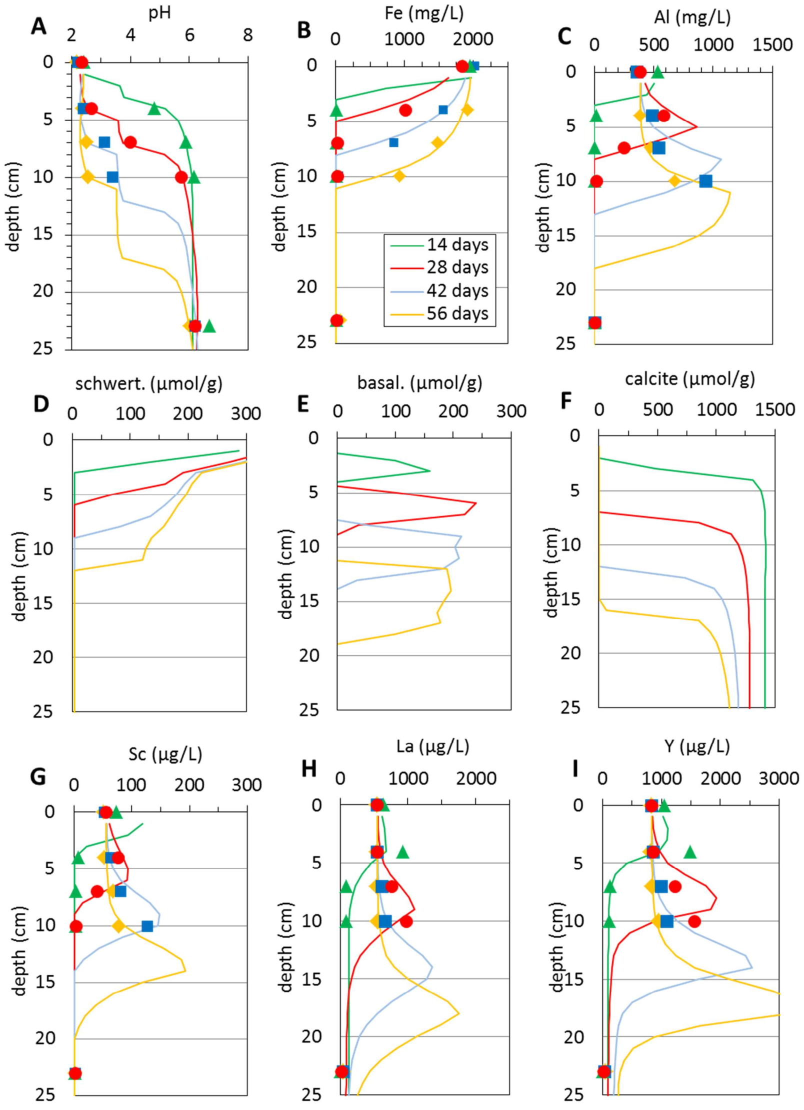

Figure 3.6 Depth profiles of experimental data (symbols) and the reactive transport model (lines) at four different stages of column operation: (A) pH evolution; (B, C) Fe and Al concentrations in pore water; (D, E, F) mineral distributions; (G, H, I) concentrations of selected REE in pore water.

3.2.1 Yttrium species in waste samples from passive treatments

The k^3-weighted EXAFS of the samples from other two laboratory-scale columns of passive remediation systems of the two AMD waters (Monte Romero:W-MR-C1-4, W-MR-C1-5 and Almagrera: W-Alm-C3-8, W-Alm-C3-9) and their Fourier transform (FT) envelope functions with corrected phase shifts are shown in Figure 2.6. The waste samples were selected from the depth where the major proportion of Al precipitated, assuming basaluminite precipitation. Visual comparisons of the EXAFS spectra of the column samples reveal a strong similarity between them, suggesting similar local order of Y in all the samples. In addition, the EXAFS spectra of the column samples are very similar to those of the solid references (B-YSO_4-ads, B-Y-ads, B-Y-cop, and A-Y-ads). They have a shoulder at ~6.5 $Å^{-1}$, indicating a higher frequency, which is absent in the aqueous samples (see the arrow in Figure 2.6).

The results of LCF of the waste samples with B-YSO4-ads and YSO4-sol references show that more than 72% of Y adopts a local geometry similar to that of the B-YSO4-ads reference (with the exception of sample W-Alm-C3-8). Thus, the majority of Y solid speciation present in the Al-rich waste from column treatments is expected to form monodentate-inner sphere complex with basaluminite surface, as indicated the best fit of the B-YSO4-ads EXAFS signal (Table 2.1), and which in turn is consistent with the sorption model of REE onto basaluminite.

Table 3.2 Percentages of Y species in the column samples obtained from LCF of the EXAFS spectra

Standard	W-MR-C1-4	W-MR-C1-5	W-Alm-C3-8	W-AlmC3-9
B-YSO4ads	0.719 ± 0.036	0.867 ± 0.038	0.495 ± 0.059	0.746 ± 0.061
YSO4-solution	0.281 ± 0.069	0.133 ± 0.071	0.505 ± 0.084	0.254 ± 0.085
R-factor	0.14	0.14	0.29	0.30
χ2	133	154	371	392

3.3 REE mobility in natural attenuation of AMD

The REE partition between aqueous and solid phase from samples of the two field sites are modeled assuming sorption onto basaluminite due to the higher concentration measured in samples with basaluminite as the major solid phase. According to Eq. 3.1, the REE concentration of the aqueous phase (and its aqueous speciation, a_{Mz+}) and the free sorption sites (obtained from the total sorption sites) were needed to predict the REE concentration in the solid phase, which were calculated from the acidic inputs.

The aqueous phase of coexisting with the basaluminite precipitates at the mixing points from the Odiel-Tinto localities contains very low amount of REE. This is because practically all the REE content of the acidic tributaries was already transferred to the solid particles, and the aqueous phase is mainly formed by the main flow of neutral water carrying precipitates in suspension. Therefore, the coexisting water is not considered in equilibrium with the solid phase, and the REE concentration of the acidic stream is used as base to calculate the activity of the aqueous species in all cases. In the case of Arroyo del Val, where the acidic water is the main flow, only a minor dilution took place and the acid water upstream the mixing was used in the calculations. To estimate the total sorption sites it was assumed that the Al transferred from the acid water to the solid phase and then converted stoichiometrically into basaluminite.

Both, the calculated and measured REE concentration in the solid phase were normalized to the NASC standard (Gromet et al., 1984) and compared. The predicted REE concentrations were always higher than the observed. This could be due to several uncertainties, such as the estimation of the sorption sites from the drop in Al concentration, the specific surface area or the effect in the concentration by the dilution by the neutral stream. Another uncertainty is the pH value at which sorption occurrs. According to the sorption variation with pH calculated with the model, the different REE undergo very different sorption efficiency at a particular pH (Figure 3.4). REE distribution pattern is highly dependent on the sorption pH. In order to facilitate the comparison of the measured and calculated REE patterns, the calculated concentrations are arbitrary multiplied by a factor f until both observed and calculated G values coincide.

The final calculated patterns were obtained by selecting manually the factor f and pH values that allow a better fit between predictions and observations (Figure 3.7). The main trends of REE distribution of the water are transferred to the solid phase but the REE concentrations predicted by the model are always higher than those observed (i.e. f<1). The f value lower than 1 indicates that the sorption sites of basaluminite surface calculated from the Al removal from the liquid phase are overestimated. This overestimation could be in part due to the fact that the solid phase is not pure basaluminite, and this has been accounted by correcting the f factor with the fraction of basaluminite in the solid (calculated from its Al concentration).

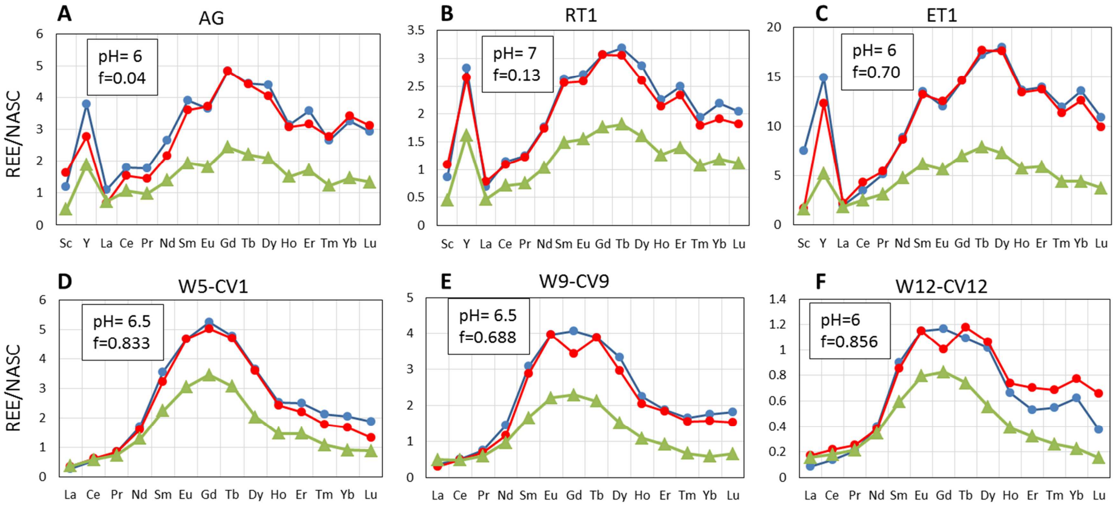

Figure 3.7 REE patterns of precipitates analyzed (red) and predicted (blue) of the parent AMD (green triangles). All the concentrations normalized to North American Shale Composite (NASC). (A, B, C) Samples from Odiel-Tinto site, (D, E, F) Samples from Arroyo del Val site.

The dilution fraction calculated from sulfate gives results comparable to the f factor.). Thus, the f value is very low (f<0.05) in the cases where the acidic stream is mixed with a predominant neutral stream (PO, AG, DB, TO), and it increases to values from 0.1 to 0.2 when the mixing streams are slightly more compensated (RT). The consistency of the f factor with sulfate dilution suggests that dilution of the acidic water may play a major role in the REE concentration in basaluminite.

However, since dilution of the acid water would also affect the Al concentration, no overestimation of the basaluminite sorption sites with respect to the REE dissolved should be expected. An explanation for low f values could be that the precipitation of Al and the REE sorption are not synchronous, especially in cases with high neutral flows (such as Odiel river cases). Thus, basaluminite starts to form earlier as pH increases above 4, whereas a significant REE sorption starts at pH values between 5 and 7. In a stream flow setting, part of the flocculates could have been dispersed and did not contact with REE aqueous species at the pH value efficient for sorption. This is consistent with the high pH values of sorption deduced from the REE patterns. Thus, the best fit of the

LREE and HREE patterns are generally obtained for sorption calculated at pH 6 or 7, values clearly higher than the onset of basaluminite precipitation.

According to laboratory experiments (Figure 2.3 B), sorption on schwertmannite occurs at pH higher than 3.5, and consistently, no Sc was detected in three samples of schwertmannite precipitates. This suggests that no Sc would be scavenged in the schwertmannite precipitates frequently covering the bed of many acid streams. Scandium samples from the Odiel-Tinto area showed no systematic differences between calculated and measured concentrations, with the exception of those from Mina Esperanza treatment (ET). There, the model systematically overpredicted the Sc concentration in the outflow of the treatment system. This indicates that the Sc from the acid water was not entirely retained in the basaluminite precipitates. Indeed, as observed in a column experiment emulating an AMD treatment with limestone, part of the Sc remained adsorbed on the solid phase whereas the rest of REE were completely mobile when the acid water front progressed in the treatment. Similar preferential fractionation of Sc to the solid phase at lower pH values was observed when neutralizing a leachate from a coal waste with NaOH (Zhang and Honaker, 2018).

4 General conclusions

The main goal of this thesis has been to understand the mechanism of REE retention in basaluminite and schwertmannite minerals that precipitates in AMD passive remediation systems and in mixing zones of AMD with neutral waters. Answering or developing a sum-up of the goals highlighted at the beginning of the thesis, we highlight the following general conclusions:

Batch sorption experiments show that basaluminite and schwertmannite can scavenge REE through sorption mechanism. The REE sorption is highly dependent on the pH and it becomes effective for Y and lanthanides from around pH 5 and for Sc from around one pH unit lower in both minerals. Lanthanide fractionation occurs in basaluminite and schwertmannite precipates, yielding and HREE enrichment onto the solids. These results are analogous to the fractionation observed in Al and Fe oxide precipitates in the confluence of the AMD waters with natural streams and rivers.

A non-electrostatic surface complexation model has been proposed to explain the sorption mechanism. In the model description, sulfate plays a key role due to its strong complexation with REE leads to sorption of the aqueous sulfate complex MSO_4^+, rather than the free ion M^{3+}, as commonly described by other authors for REE sorption in oxides. Only Sc presents important fraction of aqueous $ScOH^{2+}$ at low sulfate concentrations and also is accounted in the sorption modeling. The equilibrium constants are validated with experiments with low sulfate concentration (0.5 to 2 mM) and a different solid:liquid ratios (0.5-2 g/L) and the sorption model reproduces the sorption at different experimental conditions.

The model describes sorption of lanthanides and yttrium as the exchange of one proton from the basaluminite surface, and as the exchange of two protons from schwertmannite surface with the aqueous sulfate complexes. Thus, the MSO_4^+ aqueous species form monodentate surface complexes with basaluminite and bidentate with schwertmannite. In the case of Sc, both $ScSO_4^+$ and $ScOH^{2+}$ form bidentate surface complexes with the two minerals.

The results of the PDF and EXAFS analysis and AIMD simulations describe the formation of a monodentate inner sphere ion-pair between the Y and the S, with an interatomic distance of 3.5 Å for the YSO_4^+ aqueous complex.

The EXAFS fitting and PDF results of YSO_4 adsorbed onto basaluminite confirmed the strong interaction and the formation of inner-sphere complex between Y and basaluminite surface, as the sorption model described an exchange MSO_4^+ with one surface proton. However, EXAFS technique by itself cannot confirm the presence of the aqueous YSO_4^+ sorbed into its surface due to the low sensitivity to discern between Al and S neighbors.

The ageing experiments show that basaluminite is a metastable precipitate and its ageing in/near neutral waters can trigger its transformation into more stable Al hydroxide phases. However, basaluminite tends to stabilize when sulfate is present in solution, inhibiting its transformation to nanoboehmite. Moreover, the local structure of basaluminite is identical to $Al(OH)_3$ and sulfate is incorporated into the $Al(OH)_3$ without any effect on the its local structure. The evolution of pure basaluminite with increasing pH, releasing sulfate into solution and transforming into nanoboehmite, would result in REE release or restructuration into the surface.

The sorption model combined with a transport model 1D successfully predicts the evolution of aqueous REE analyzed from the pore water of a laboratory column simulating a passive remediation system. The model explains the REE enrichment in the Al waste due to the preferential sorption of Y and lanthanides on basaluminite. The model also shows the behavior of Sc which at lower pH remains preferentially retained in schwertmannite precipitates. Although schwertmannite and basaluminite have similar sorption edges, Y and the lanthanides only sorb at pH values higher than 4.5, and sorption only occurs on basaluminite because schwertmannite forms at pH values lower than 4. In contrast, the Sc sorption edge extends from pH 3 to 5 and therefore can partially sorb on schwertmannite.

The aqueous and solid samples recovered from field also show REE mobility dependent on the pH. When an AMD mixes with an alkaline stream, a mixture of schwertmannite and basaluminite precipitate. The behavior of REE during the mixing is conservative at low pH ($pH<3$), whereas they are scavenged by the flocculates at near neutral pH. This confirms the observations made by previous studies and suggests that Al-phases could be responsible for REE retention. When Fe and Al phases can be sampled separately, schwertmannite does not contain REE, which are entirely retained in basaluminite, confirming that basaluminite phase is the main responsible for the REE removal.

The sorption model applied with basaluminite surface is able to anticipate the main trends of the REE distribution patterns observed in the Al-rich solids recovered in the field sites, regardless the sulfate concentration in the acid drainage. The distribution patterns confirm the selective sorption of MREE, HREE and Y with respect to LREE.

The sorption model presents, however, some uncertainties in the modeling of the REE sorption of the field solids. First, the amount of basaluminite particles (and sorption sites) that would form from the Al dissolved in the acid stream can be diluted-dispersed in the mixture. Nonetheless, the dilution factor could be independently approximated from other conservative solutes.

A second uncertainty is the estimation of the pH at which sorption occurs. This pH could be approached from the geochemical modeling of the major element chemistry and flow proportions of the two end members. All these calculations assume that all the reactions occur in a close system. However, if reactions are not synchronous in an open flow setting total masses may not be conservative. Thus, basaluminite starts to form earlier as pH increases above 4, whereas the significant REE sorption occurs at pH values between 5 and 7, where some basaluminite could has been transported away. This precludes an accurate modeling of the REE concentrations of the solid phase.

Finally, scandium adsorbs in the solid particles at pH one unit lower than the rest of REE, but it seems to behave as the rest of REE in acid streams of pH below 4. Therefore, no Sc would be scavenged in the schwertmannite precipitates frequently covering the bed of many acid streams, and it could be partially recovered in the treatment plants as the rest of REE.

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6 Annex

Article 1

Local structure and ageing of basaluminite at different pH values and sulphate concentrations

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Local structure and ageing of basaluminite at different pH values and sulphate concentrations

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Felsöbányaite

A B S T R A C T

Basaluminite is a poorly crystalline aluminium sulphate oxyhydroxide that precipitates in acid mine drainage waters and acid sulphate soils when pH increases above 4.5 approximately. The pH increase can be due to mixing with natural waters or by the addition of an alkaline reagent, a method commonly used in remediation treatments. Basaluminite is a scavenger of elements such as Se, As, Sb, Mo, P and rare earth elements (REEs) and acts as a vector for their transport in the environment. The retention of these elements has important environmental and economic impact due to their toxicity and to the potential extraction of REEs for technological applications. Despite the long history of basaluminite, initially described as a mineral in the late 40s, little is known about its stability and its eventual transformation in other less metastable phases. Here, the stability of synthetic basaluminite in aqueous solutions with different pH values and sulphate concentrations was studied for 81 days. Chemical analyses of the aqueous phase combined with High-Energy X-ray Diffraction and Pair Distribution Function (PDF) analyses of the solids were used to characterize the ageing process. In contact with water, basaluminite incongruently dissolves, precipitating amorphous Al-hydroxide and releasing sulphate to the solution. This process and the recrystallization of amorphous Al-hydroxide into nanoboehmite were enhanced with increasing pH. However, for high SO_4 concentrations, such as those found in acid mine waters, the transformation to nanoboehmite was partially inhibited. The ageing processes highlighted here point to a potential pathway for the desorption of trace elements upon neutralization of acid mine drainage. Furthermore, PDF analyses of basaluminite show a high similarity with the local structure of a synthetic amorphous Al-hydroxide.

1. Introduction

Hydrobasaluminite and basaluminite were first described as white precipitates from an ironstone mine (Bannister and Hollingworth, 1948; Hollingworth and Bannister, 1950). These precipitates have appeared together with allophane and other clay minerals. A difference between these materials was based on their water content, i.e., the water content is higher for hydrobasaluminite. Hydrobasaluminite, $(Al_4(SO_4)(OH)_{10}{\cdot}16\text{-}34H_2O)$, has been described as a white clay-like mineral, which losses water molecules yielding basaluminite, $(Al_4(SO_4)(OH)_{10}{\cdot}5H_2O)$, with a characteristic fine powder aspect and very broad diffraction peaks. Since then, most reports of basaluminite have been made from precipitates occurring in acidic sulphate-rich waters (Van Breemen, 1973; Adams and Rawajfih, 1977; Nordstrom, 1982; Bigham and Nordstrom, 2000) when the solution pH value increases in a range 4.0–4.5 due to mixing with natural waters or after the addition of an alkaline reagent, a common practice in treatment systems. Basaluminite, similar to its Fe(III)-bearing counterpart schwertmannite, is known for its high capability to retain both silica and toxic elements such as Se, As, Mo, Cr, Sb, V, Pb, U and P (Nordstrom and Alpers, 1999; Bigham and Nordstrom, 2000; Fukushi et al., 2004; Sibrell et al., 2009; Sánchez-España et al., 2016; Carrero et al., 2017a). Both precipitates are important phases in the waters where they are present due to their high reactivity with strong environmental implications. On the other hand, basaluminite and schwertmannite are responsible for the uptake of high concentrations of Rare Earth Elements (REEs) in acidic streams (Verplanck et al., 2004; Gammons et al., 2005). This process affects drastically the lanthanides partition pattern in these waters, impacting geochemical studies based on lanthanide distributions. Moreover, basaluminite has been proven to retain Sc, Y and lanthanides when it

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precipitates in passive remediation systems of acid mine drainage (Ayora et al., 2016). In these systems, AMD waters are neutralized using a reservoir of $CaCO_3$, reaching pH values higher than 6 in the output. The REE contents in the precipitated basaluminite are estimated to be approximately 2 to 12 μmol/g, depending on the initial REE water content, and represent an opportunity to recover REEs from basaluminite. These water treatment systems can work for several months to years with a constant pH evolution. Thus, a detailed characterization of the stability of basaluminite at different solution pH values becomes essential.

Literature reports on the structure of basaluminite are confusing. The first structure was proposed by Clayton (1980) from X-ray powder patterns using samples derived from acid water resulting from the oxidation of pyrite. These earlier studies described broad diffraction peaks such as those expected in nanocrystalline phases. However, a more recent report based on single-crystal X-ray diffraction (Farkas and Pertlik, 1997) gave unit cell parameters and atomic positions of basaluminite and felsöbanyáite, establishing that the first is just a nanocrystalline version of the second. This fact is confusing for two reasons: (i) the basaluminite formed in AMD is typically very disordered, and the occurrence of single crystals has never been reported; and (ii) felsöbanyáite is a rare mineral, never reported in AMD. As indicated by Carrero et al. (2017b), the similarity between the structures of basaluminite and felsöbanyáite could be due to a simple fortuitous coincidence. These authors used High-Energy X-ray Diffraction (HEXD) with Pair Distribution Function (PDF) analyses and Extended X-ray Absorption Fine Structure (EXAFS) to describe the local order in synthetic and natural (from AMD) basaluminite samples. The authors confirmed the Al-octahedral framework of the structure with sulphate coordinated as outer-sphere ligands, as previously proposed by Farkas and Pertlik (1997). Regarding its stability, some experiments where synthetic basaluminite aged in its mother solution showed that the mineral partially or totally recrystallizes with temperature forming alunite, depending on the conditions (Adams and Rawajfih, 1977; Prietzel and Hirsch, 1998). Therefore, the basaluminite formed in solution can be considered a metastable solid in a wide range of pH values, the formation of alunite being kinetically retarded (Nordstrom, 1982; Prietzel and Mayer, 2005).

In a more recent study of the solubility Al-solids based on chemical analysis and EXAFS spectroscopy, Jones et al. (2011) indicated that the synthetic and natural precipitates consisted of a mixture of basaluminite and amorphous $Al(OH)_3$ when the solution pH was approximately above 4.5, and the major phase present at pH 7 was basaluminite instead of $Al(OH)_3$ with adsorbed sulphate. Jolivet et al. (2011) proposed that amorphous $Al(OH)_3$ can recrystallize to gibbsite, bayerite or boehmite depending on pH and/or temperature. Similarly, recent SEM/TEM studies by Sánchez-España et al. (2016) have documented the coexistence of basaluminite globules with nanocrystals of $Al(OH)_3$ (gibbsite, bayerite) and allophane in natural Al precipitates formed at pH 4.0–4.5 in pit lakes. Based on the textural findings observed by SEM and TEM, these authors concluded that the nearly amorphous basaluminite globules partly transformed to gibbsite or bayerite during ageing. However, no ageing with detailed structural studies have been undertaken to confirm the transformation of basaluminite to more crystalline forms and to determine the parameters that control such a transformation.

The objective of the present work is to study the stability of basaluminite during ageing. Since basaluminite is a mineral that precipitates in acidic and rich sulphate waters, the second objective is to understand the role of pH and aqueous SO_4 in its stability. To achieve this, two set of suspensions of pure synthetic basaluminite were maintained in contact with solutions at different pH values and sulphate concentrations along different time spans. The resulting aqueous and solid phases were carefully characterized.

2. Materials and methods

2.1. Samples and experimental protocol

2.1.1. Pure solid synthesis

Basaluminite was synthesized following the method described by Adams and Rawajfih (1977), i.e., by adding 214 mL 0.015 M $Ca(OH)_2$ to 30 mL 0.05 M $Al_2(SO_4)_3 \cdot 18H_2O$ (both commercial reagents). The synthesis was performed by drop-by-drop addition, until an OH:Al molar ratio of 2.14 was reached under continuous stirring and at room temperature. The solid was washed three times to remove co-precipitated $CaSO_4 \cdot 2H_2O$ and dried 48 h at a maximum temperature of 40 °C.

Moreover, two $Al(OH)_3$ precipitates were synthesized in the laboratory to be used as references. The method described by Xu et al. (2011) was used, i.e., a 1 M NaOH solution was titrated into a 0.5 M $AlCl_3 \cdot 6H_2O$ solution. The titration was conducted by drop-by-drop addition until pH values of 8.1 and 7.3 were reached for each precipitate (samples labelled $Al(OH)_3$_pH 8 and $Al(OH)_3$_pH 7, respectively). The first solid (pH 8.1) was washed three times with deionized water and directly dried for 72 h at $T = 40$ °C. The second precipitate (pH 7.3) was washed seven times with deionized water, directly frozen and then lyophilized.

Digestion of 0.1 g of synthetic basaluminite in 5 mL HNO_3 65% was carried out for 12 h at 115 °C for chemical characterization. Systematic XRD analyses were conducted for all the synthetic solids to dismiss impurities.

2.1.2. Fast ageing experiments (high solid:liquid ratio)

A set of kinetic experiments was performed to understand the evolution of basaluminite solubility over a short period of time. To ensure the quantification of sulphate and aluminium in the aqueous phase by ICP-AES, a solid:liquid ratio of 1:1 was selected. However, only a minor fraction of the initial solid was expected to transform with such a high solid:liquid ratio. Thus, the set consisted of 10 suspensions of 10 mg of synthetic basaluminite in 10 mL of a 0.01 M $NaNO_3$ solution with a pH value of 5.8. The suspensions were aged for different short periods of time: 5, 10, 15, and 35 min and 1, 2, 6, 18, 48 and 96 h. At different times, each suspension was filtered to 0.22 μm, the pH was measured, and the solutions were acidified with HNO_3 65% for further chemical analyses of Al and SO_4.

2.1.3. Slow ageing experiments (low solid:liquid ratio)

A solid:liquid ratio of 1:10 was selected in this case to ensure that most of the initial solid was transformed at the end of the experiment, although some SO_4 and/or Al concentrations remained below detection levels. A set of 12 suspensions of 5 mg of synthetic basaluminite in 50 mL 0.01 M $NaNO_3$ solution was first equilibrated during 48 h with continuous stirring at room temperature. After this period, the pH was measured, and the suspensions were centrifuged at 4500 rpm for 10 min. An aliquot of 5 mL of the supernatant was collected, filtered to 0.22 μm and acidified with HNO_3 65% for further chemical analysis. Then, different amounts from 10 to 100 μL NH_4OH 0.5 M were added to reach initial pH values ranging between 4.9 and 9.2. The suspensions were aged under continuous stirring for 81 days. During this period, pH measurements were performed periodically. After this time, the suspensions were centrifuged at 4500 rpm for 10 min. Aliquots of supernatants were taken, filtered to 0.2 μm and acidified with HNO_3 65% for further chemical analysis. The solids were dried for 48 h at a temperature of 40 °C. These series of experiments were duplicated, and the average of the results from the two experiments is presented.

Another set of 12 suspensions was prepared, but in this case, the initial solution also contained 0.02 M Na_2SO_4. The same procedure, as described in the previous paragraph, was followed, although the pH values of the starting solutions after adding different amounts of NH_4OH were lower and ranged between 5.08 and 6.16. The reproducibility of the experiment was confirmed by multiple runs at the highest pH (n = 4). This pH was chosen because it is the value at which larger changes in the solid are expected.

2.2. Analytical techniques

2.2.1. Aqueous phase analysis

Measurements of the initial and final pH solutions were made with a Crison® glass electrode calibrated with buffer solutions of pH 2, 4, 7 and 9. Sulphur, Al, and Na were measured by ICP-AES (Thermo Scientific – iCAP 6500, Radial acquisition). Certified solutions (CPI International-CCV standard 1-solution A) were intercalated within the samples to check the analytical accuracy. The detection limits were 1.6, 1.0 and 4.3 μmol/L for S, Al and Na, respectively. The analytical precision error was estimated to be approximately 2%.

Aqueous speciation and saturation indices of the solutions were calculated with PHREEQC code (Parkhurst and Appelo, 1999) using the WATEQ4F database (Ball and Nordstrom, 1991).

2.2.2. Solid phase analysis

The X-ray Diffraction (XRD) patterns of the solid phases were obtained by a Bruker D8 A25 Advance diffractometer θ-θ with $CuK\alpha_1$ radiation. The diffractometer operated at 40 kV and 40 mA in a Bragg-Brentano geometry and was equipped with a linear LynxEye XE detector. The diffractograms were obtained from 4 to 60° in 2θ with a step size of 0.015° and a counting time of 0.1 s.

Thermogravimetric analyses (TGA) were performed to determine the water content of basaluminite from loss vs. temperature curves using a Mettler Toledo TGA/DSC3 + instrument with a N_2 flow rate of 20 mL/min. The temperature increased from room temperature to 900 °C at a rate of 10 °C/min. To this end, a few mg of each sample were loaded into alumina crucibles.

High Energy X-ray Diffraction (HEXD) experiments and Pair Distribution Function (PDF) analyses were performed at beamline ID31 at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Powder samples were loaded into polyamide capillaries. Scattering from samples and from background (empty capillary) were measured at room conditions and at 68.5 keV (λ = 0.181 Å) incident X-ray energy, which was calibrated using a CeO_2 standard (NIST 674b). The 2D images collected with a flat panel Pilatus3 XCdTe 2 M detector were corrected and integrated using pyFAI (Kieffer and Karkoulis, 2013). Structure factors S(Q) and PDFs were obtained using PDFGetX3 software (Juhás et al., 2013).

The resulting coherent scattered intensity, $I(Q)$, from the HEXD data is given by the Debye equation Eq. (1) and plotted as a function of the magnitude of the scattering vector Eq. (2) (Dinnebier and Billinge, 2008):

$$I(Q) = \sum_{m,n}^{N} f_m(Q) f_n(Q) \frac{sin(Qr_{mn})}{Qr_{mn}} \tag{1}$$

where f_m and f_n are atomic scattering factors and r_{mn} is the distance between a pair of atoms m and n. The scattering vector, Q, is described as follows:

$$Q = |Q| = 2ksin\theta = \frac{4\pi sin\ \theta}{\lambda} \tag{2}$$

The scattered intensity, $I(Q)$ is divided by the number of the scatterers, N, and the average scattering per atom, which is the square of the atomic form-factor, $\langle f \rangle^2$, Eq. (3):

$$\langle f\rangle^2 = \left(\sum_i c_i f_i\right)^2 \tag{3}$$

where c_i is the concentration of the element i, and f_i its atomic form factor. The total structure function or structure factor, $S(Q)$, is then obtained Eq. (4). In this work, the structure factors as a function of 2θ are shown.

$$S(Q) = \frac{I(Q)}{N\ \langle f\rangle^2} \tag{4}$$

The representation of the scattering data in real space allows an easier interpretation of the short-range order and comparison with other mineral or amorphous compounds. To do so, a Fourier Transform to real-space is performed and a Pair Distribution Function (PDF) is obtained. This function, also called $G(r)$, displayed in Eq. (5), represents the probability of finding pairs of atoms separated a distance, r:

$$G(r) = \frac{2}{\Pi}\int_0^{\infty} Q[S(Q) - 1]\sin(Qr)dQ \tag{5}$$

Linear Combination Fitting (LCF) analyses were conducted for the PDFs of solids recovered at the end of the experiment using synthetic pure standards. The LCF tool from the Athena IFFEFIT package (Ravel and Newville, 2005) was used to this end. A combinatory study of these standards was performed, and the best fit in terms of the R-factor was selected, Eq. (6). The factors obtained from the model represent the fraction of each standard needed to better describe the unknown sample. The model represents the least square fit to the sample spectrum. The relative weights of the components of the mixture can vary from 0 to 1 and are forced to sum to 1. An R-factor was calculated, where X_i is the set of variables:

$$R = \frac{\sum_i^{N_{fit}} [\chi_i^{data} - \chi_i^{model}(x)]^2}{\sum_i^{N_{fit}} [\chi_i^{data}]^2} \tag{6}$$

3. Results

3.1. Pure synthetic solids

3.1.1. Chemical characterization

The solid digestion and TGA analysis of the synthetic basaluminite yielded the formula $Al_4(SO_4)_{1.25}(OH)_{9.50}{\cdot}4.75H_2O$ with a higher sulphate content than the stoichiometry of $Al_4(SO_4)(OH)_{10}{\cdot}5H_2O$, reported by Hollingworth and Bannister (1950) and Farkas and Pertlik (1997). The TGA data showed a sigmoidal-like water desorption and decomposition step (Fig. S1) similar to that described in Carrero et al. (2017b). The weight loss observed between 150 °C and 342 °C is due to the vaporization of physisorbed H_2O and structural OH/H_2O.

3.1.2. Structural characterization

The XRD patterns of the synthetic pure solids obtained with $CuK\alpha_1$ X-ray source are shown in Fig. S2. The basaluminite and $Al(OH)_3$_am at pH 7 samples show low-angle peaks and a large peak covering the range from 35 to 50°. The $Al(OH)_3$_am at pH 8 shows five very large peaks that correspond to the (020), (120), (031), overlapping (051) and (200), and (231) reflections of boehmite (γ-AlOOH) (Fig. S3, obtained with synchrotron HEXD data). The very broad width of these peaks suggests nanocrystalline boehmite. From here on, the two $Al(OH)_3$ samples will be labelled Al(OH)3_am (sample synthesized at pH 7.3) and nanoboehmite (sample synthesized at pH 8.1).

The PDFs for basaluminite, $Al(OH)_3$_am, nanoboehmite, and the two aged samples of $Al(OH)_3$_am and nanoboehmite (samples stored under atmospheric conditions and measured one month later) are displayed in Fig. 1. The two synthetic nanoboehmite samples show a higher degree of crystallinity than that of the amorphous and basaluminite samples. This crystallinity is reflected by the coherent domain size, which is approximately 10 Å for basaluminite and fresh amorphous $Al(OH)_3$ and increases to at least 25 Å for the aged samples. Individual atomic pairs can be identified in the PDFs. The peak at 1.49 Å in basaluminite corresponds to the S—O bonds. The remainder of the main peaks in the

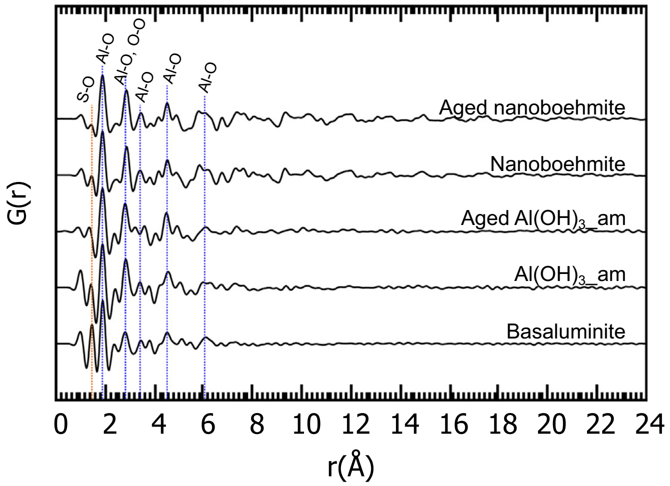

Fig. 1. PDFs of synthetic basaluminite, $Al(OH)_3$_am and nanoboehmite. $Al(OH)_3$_am and nanoboehmite were measured after one month, and a slight recrystallization is observed. Data are normalized to the Al-O peak.

three standards, corresponding to Al—Al, Al—O and O—O distances, are placed in the same positions for all the samples. The Al—O bond has an interatomic distance of 1.88 Å. Both Al—Al and O—O interatomic distances overlap and have the same interatomic distance of 2.8 Å. The peaks at 3.6, 4.6 and 6 Å are due to the Al—O distances. Differences in the relative peak intensities are due to the presence of point defects.

3.2. Fast ageing experiment

Prior to describe the ageing experiments, it is interesting to remark that the initial pH of the suspension depended on the solid:liquid ratio. Thus, the pH values of two suspensions of 10 mg of basaluminite in 10 and 100 mL of a 0.01 M $NaNO_3$ electrolyte solution after 2 h were 4.31 and 4.98, respectively. This effect is more evident if an amount of OH^- is added to raise the initial pH. Thus, NH_4OH was added to two solutions similar to those described to increase the initial pH to 10. After 2 h, the pH values of the solutions were 4.60 and 8.69 for solid:liquid ratios of 1.1 and 1:10, respectively. Moreover, the initial pH also depends on the amount of sulphate in the suspension. Thus, the pH values of two 1:1 suspensions without and with 0.02 M Na_2SO_4 after 2 h were 4.31 and 4.69, respectively. These features suggest a strong basaluminite-solute interaction.

Ten suspensions of 10 mg of basaluminite were in contact in 10 mL of a 0.01 M $NaNO_3$ background electrolyte solution. After the first five minutes, the pH decreased to 4.02 and then after 2 h, the pH increased to 4.31. From 2 to 96 equilibrating hours, the pH was maintained at a constant value of 4.30 ± 0.034 (Fig. 2A). The equilibrium conditions for ageing experiments were considered after 48 h.

During the time studied, the dissolved SO_4 was highly correlated with Al ($R^2 = 0.99$), which resulted in a SO_4:Al ratio of 1.40, (Fig. 2B) but also Al correlates with H^+ ($R = 0.71$) in a H^+:Al ratio of -0.19 (Fig. 2C), suggesting a basaluminite-water reaction that will be discussed below. The saturation index for basaluminite, boehmite, gibbsite ($Al(OH)_3$) and amorphous gibbsite are shown in Table S1 in Electronic Annex. At the beginning, the solution was undersaturated with respect to these phases but quickly reached supersaturation in basaluminite, gibbsite and boehmite.

3.3. Slow ageing experiments

3.3.1. Aqueous phase

Twelve suspensions of 5 mg of synthetic basaluminite in 50 mL of a 0.01 M $NaNO_3$ background solution were equilibrated for 48 h. After this time, the average solution pH for the twelve points was 4.98 ± 0.10, and the chemistry was 0.042 ± 0.001 mmol/L Al, 0.074 ± 0.002 mmol/L S and 10.030 ± 0.201 mmol/L Na (Table S2). The experimental molar ratio of aqueous SO_4:Al was 1.79. This value greatly differs from 0.31, the stoichiometric ratio expected from congruent dissolution, as will be discussed below. All the solutions were supersaturated with respect to basaluminite and undersaturated with respect to amorphous $Al(OH)_3$ (Table S3).

Increasing amounts of NH_4OH 0.5 M were added to each solution to adjust the pH to values ranging from 4.95 to 9.22 (Table S4). The main OH consumption occurred mainly during the first 19 days, and the solution pH continued to decrease for 81 days (Fig. 3A). At the end of the experiment, the pH values ranged between 4.61 and 6.46. The solution pH decreased 0.5 pH units for the suspension with the lowest amount of NH_4OH added and 3.0 pH units for the solution with the highest amount of NH_4OH added (Table S4). No NH_4OH was added to the first suspension, and after the ageing time, the pH decreased only 0.34 units.

At the end of the experiment, the aqueous Al and SO_4 concentrations did not correlate with the pH. At lower pH values (4.61–5.10) the amount of sulphate remained almost constant, whereas the aluminium concentration in the solution decreased slightly (Fig. 3B). For pH values higher than 5.10, the Al in solution was below the detection limit (0.001 mM), but the SO_4 increased constantly (Fig. 3B). At the pH range 5.10 to 5.85, a linear correlation between SO_4 release and excess $[OH^-]$ was observed ($R^2 = 0.989$) with a molar ratio $OH:SO_4$ of 4.0 (Fig. 3C). The excess $[OH^-]$ was calculated from the difference between the NH_4OH added and the final measured pH value.

To understand the influence of SO_4 in the behaviour of basaluminite, the ageing experiment was repeated adding 0.02 M Na_2SO_4 to 12 new suspensions. After 48 h, the average solution pH was 5.12 ± 0.10, and the elemental concentrations were 0.01 ± 0.0003 mmol/L Al, 21.16 ± 0.423 mmol/L of S and 49.05 ± 0.981 mmol/L Na. Detailed results can be found in Table S5. All the solutions were almost in equilibrium with respect to basaluminite and undersaturated with respect to amorphous $Al(OH)_3$ (Table S6).

The same amounts of NH_4OH (0 to 100 μL 0.5 M) were added. At the beginning, the pH values rose from 5.08 to 6.16, which is much less compared with the values in previous experiments without the addition of sulphate (compare Table S4, both experiments at time 0 h). The pH continued to increase for 40 h, although these values did not reach the pH values of the experiment without sulphate (Table S5). Then, the solution pH decreased during the remaining 81 days. The final pH ranged between 5.06 and 7.18 at the end of the experiment. The final pH values decreased to between 0.8 and 1.02 units. The pH decreased only 0.02 units in the first sample of the series, to which no NH_4OH had been added. Due to the amount of SO_4 added, no correlation between the released sulphate and aluminium and excess OH^- was observed in this case.

3.3.2. Solid phase

The structure factors extracted from the HEXD patterns, S(Q), for the solids aged during 81 days in the absence of sulphate are shown in Fig. 4A. The samples at lower pH values exhibit typical broad oscillations characteristic of amorphous or poorly crystalline materials. New broad peaks appear in the patterns of the solids formed at pH values higher than 5.47, clearly defined from pH 5.85. These peaks correspond to boehmite with two possible peaks belonging to bayerite and a possibly few peaks attributed to natroalunite ($NaAl_3(SO_4)_2(OH)_6$) (Fig. 4A). The characteristic broad bands for basaluminite are no longer present at these high pH values. These observations agree with those determined by Singh (1969) in the XRD patterns obtained after ageing basaluminite with and without gibbsite along 103 days, as well as those of $Al_2(SO_4)_3$ aged for 42 months, where a mixture of boehmite, gibbsite and alunite (as natroalunite) phases was identified in Singh (1982). The small peaks in the basaluminite patterns are due to the memory effects of the 2D detector. The structure factors of the solids equilibrated in the presence of sulphate (Fig. 4B) were in general similar to the ones shown

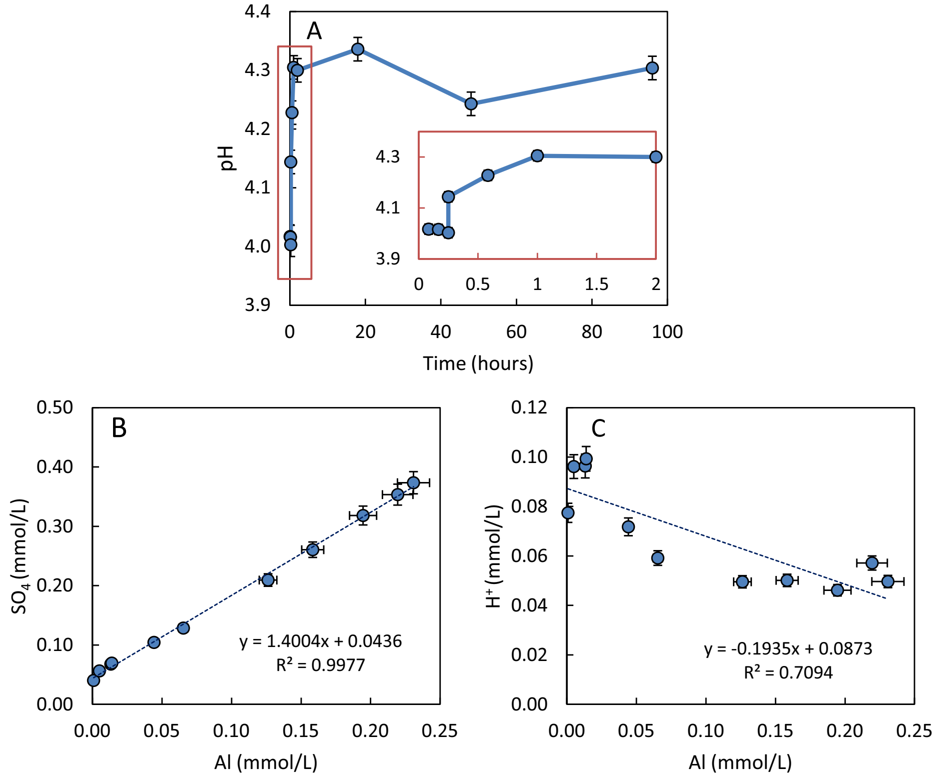

Fig. 2. (A) Evolution of pH during basaluminite stability with a background solution for 96 h. The inset depicts a magnified view of the first 2 h, where the pH increase is shown. (B) Correlation between SO_4 and Al with time. (C) Correlation between H^+ and Al with time. See the data in supporting information, Table S1.

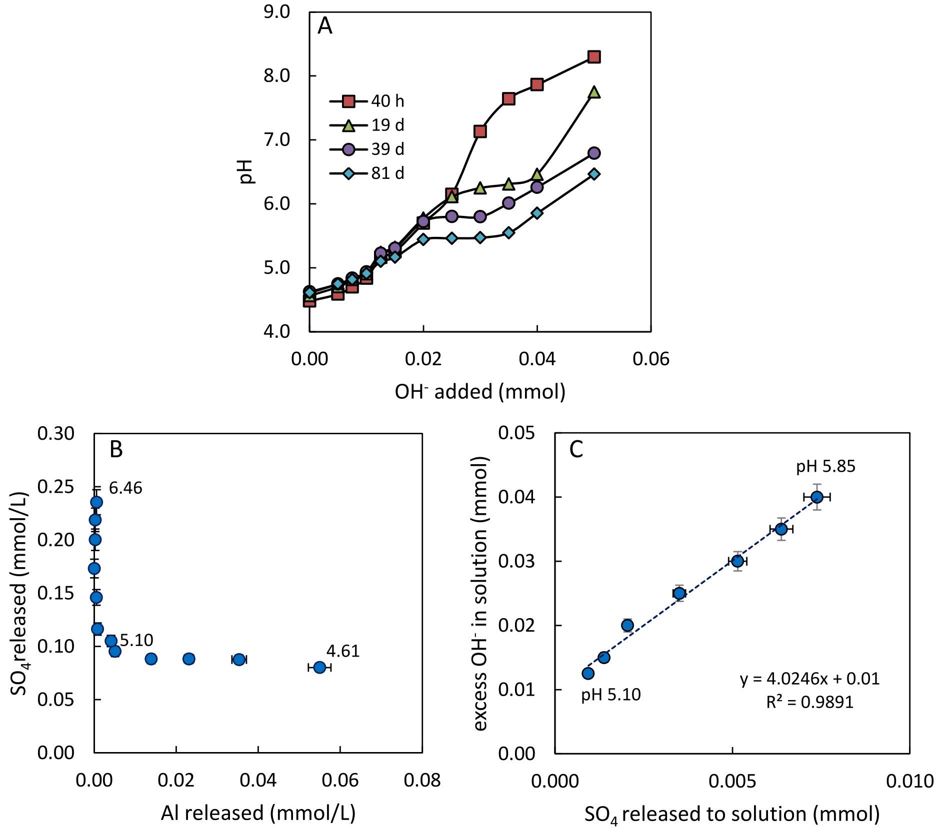

Fig. 3. (A) Evolution of pH for the suspensions with different initial pH values. (B) Aluminium and SO_4 evolution of the different suspensions after 81 days of ageing. The values depicted inside are the final pH values. (C) Correlation between the OH^- excess and SO_4 concentration for the suspensions with higher pH values. The OH^- excess is calculated as the difference between the added NH_4OH and the OH^- invested in the rising pH.

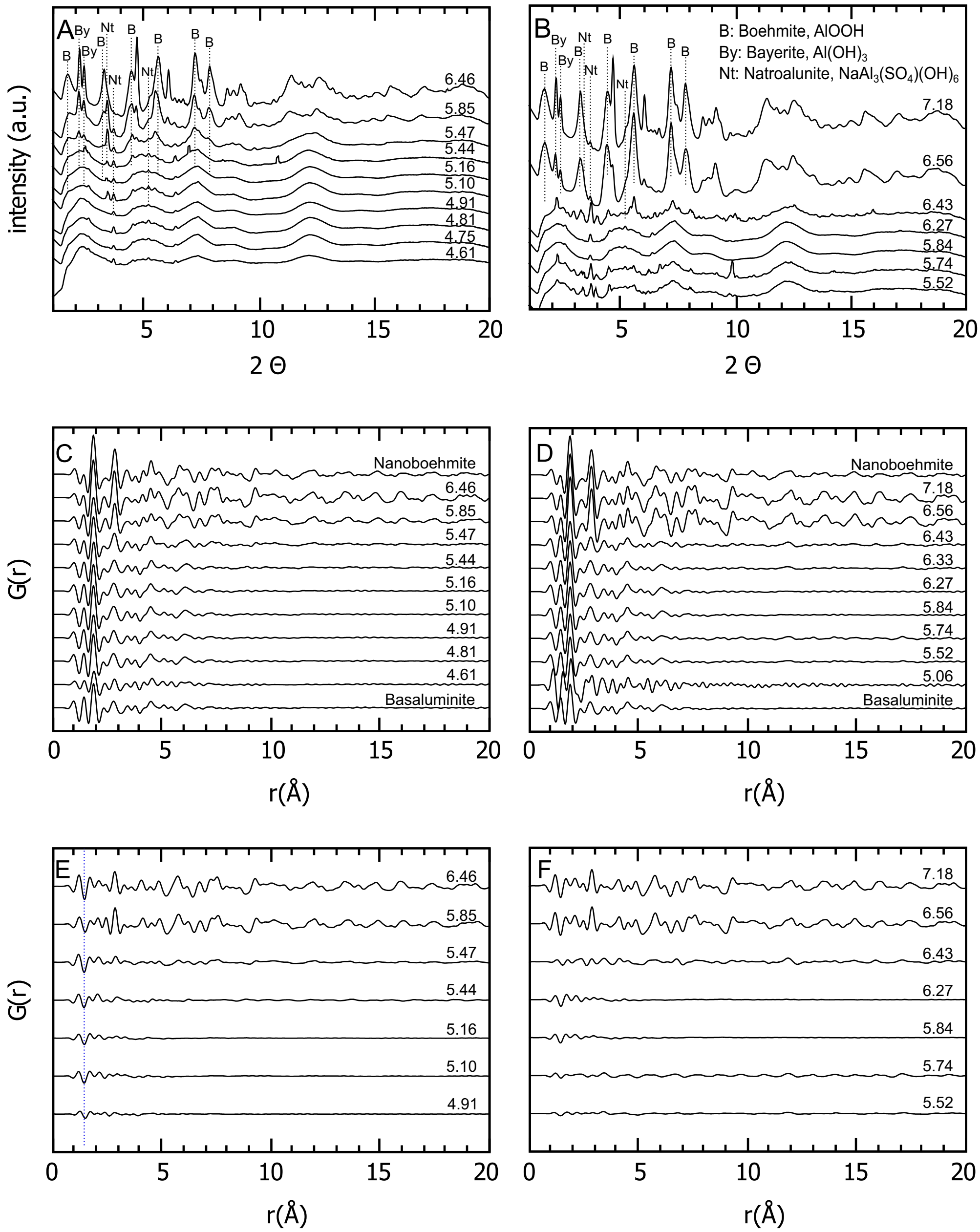

Fig. 4. Structure factors with Q converted to 2θ for the solid samples equilibrated and aged during 81 days in the absence of sulphate (A) and with an initial sulphate content (B). The wavelength of the X-rays used was of λ = 0.181 Å. (C, D) PDFs of the aged solids and synthetic nanoboehmite and basaluminite for the experiment in the absence of sulphate and with initial sulphate, respectively. (E, F) Differential PDFs for both experiments. The vertical dotted line indicates the position of the S—O bond. Negative peaks reflect the decrease in the sulphate content in the solids.

in Fig. 4A. Some peaks were identified as belonging to boehmite. From pH 6.56, the broad peaks indicate nanocrystalline boehmite, which were sharper than those for the experiment without sulphate, indicating an increase in the crystallinity. Again, residual NaAl$_3$(SO$_4$)$_2$(OH)$_6$ and some systematic peaks due to the memory effect of the detector were also present.

The PDFs of the solids equilibrated in the absence of initial sulphate in the solution together with those of pure synthetic basaluminite and nanoboehmite are shown in Fig. 4C. At lower pH values, the PDFs are very similar to the PDF of synthetic basaluminite, whereas at higher pH values, a transition to a nanoboehmite-like local structure is observed. Fig. 4D shows the differential PDF generated by subtracting the PDF of pure basaluminite from each sample. Two observations can be made: (i) a negative peak of increasing intensity (S-O peak at 1.49 Å) corresponding to the release of sulphate from the samples as the pH increases, and (ii) a transition to a more crystalline phase. The PDFs of the experiment with added sulphate show similar trends (Fig. 4E).

4. Discussion

4.1. Basaluminite ageing at different pH and SO$_4$

As stated in Section 3.1.1., the synthetic basaluminite had a S:Al ratio of 0.31, higher than the stoichiometry of 0.25 reported in the literature. In the long ageing experiments without added sulphate, 23% of the sulphate was transferred from the solid into the solution after 48 h of equilibration (Table S2), and the calculated SO$_4$:Al ratio in the residual solid reached a stoichiometric value of 0.25. This fast release of sulphate towards the stoichiometry has been interpreted as the desorption of sulphate from the outer-sphere surface complexes (Wang et al., 2015; Carrero et al., 2017b). Similar sulphate desorption was also proposed for the early ageing of schwertmannite (Burton et al., 2008). However, our fast ageing experiment showed clear correlations with SO$_4$:Al and H$^+$:Al ratios of 1.40 and −0.19, respectively (Fig. 2B, C). These relations are explained as an incongruent basaluminite

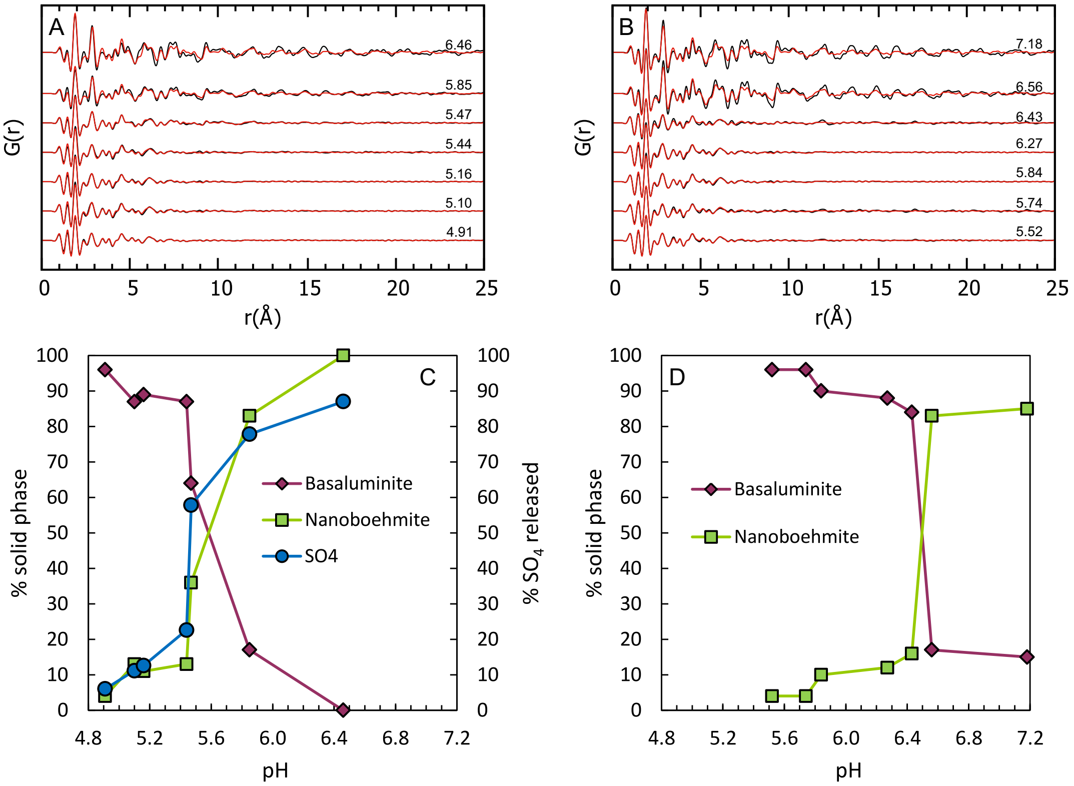

Fig. 5. (A, B) Experimental PDFs (black) and LCF fits of the PDFs (red) using pure basaluminite and nanoboehmite as end members for the fits of solids from the slow ageing experiments without initial sulphate (A) and with initial sulphate (B). (C, D) Percentages of the end members, basaluminite (rhomboids) and nanoboehmite (squares) calculated from the LCF fitting for experiments without (C) and with initial sulphate (D). Percentage of released sulphate calculated from aqueous chemistry (circles) in the experiment without initial sulphate (C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

dissolution with the subsequent Al hydrolysis and $Al(OH)_3$ precipitation, as expressed with the following process reaction:

$$Al_4(SO_4)_{1.25}(OH)_{9.5} + 0.17\,H^+ \rightarrow 0.89\,Al^{3+} + 1.25\,SO_4{}^{2-} + 3.11\,Al(OH)_3(s) + 0.17\,H_2O \quad (7)$$

Owing to the high amount of sulphate added, such a variation in sulphate concentration was not observed in the experiments where Na_2SO_4 was added to the initial suspensions.

Beyond the first 48 h, and after OH^- addition, a decrease in the pH was observed in the slow ageing experiments (Fig. 3A). This variation was more accentuated when no sulphate was added to the initial suspensions. The structure factors clearly showed that boehmite peaks appeared in the solids from the experiments with higher initial pH values (Fig. 4A, B). Concomitantly, the PDFs of these solids reflected an increase in the crystallinity at higher pH values (Fig. 4C, D). From these observations, a transformation of basaluminite to nanoboehmite with time can be inferred. This transformation was more evident when a higher amount of OH^- was added into the solution. Since the PDF spectrum at the lowest pH is very similar to basaluminite and at the highest pH to synthetic nanoboehmite, Linear Combination Fits (LCF) of the experimental PDFs were performed using these two synthetic solids as end members (Fig. 5A, B). The results of the fitting show a clear decrease in the proportion of basaluminite along with an increase in nanoboehmite as NH_4OH was added and the final pH value was higher (Fig. 5C, D). When it could be measured, this behaviour with pH is also consistent with the transfer of sulphate from the solid to the aqueous phase (Fig. 5C).

With respect to the aqueous phase, the increase in nanoboehmite in the solid phase was consistent with the amount of sulphate released from basaluminite. The molar ratio between the SO_4 released and OH^- consumed was 4 (Fig. 3C). This result can be explained by a sequence of chemical reactions involving the dissolution of basaluminite and the formation of nanoboehmite and natroalunite, $NaAl_3(SO_4)_2(OH)_6$, according to the process reaction:

$$5Al_4(SO_4)(OH)_{10}\cdot 5H_2O + 2Na^+ + 4OH^- \rightarrow 2NaAl_3(SO_4)_2(OH)_6 + 14AlOOH + SO_4{}^{2-} + 39H_2O \quad (8)$$

Since in the first 48 h, 23% of SO_4 was released, and the basaluminite stoichiometry reported in the literature was used in the reaction. The solution reached supersaturation with respect to alunite (Table S3) at expense of the Al and SO_4 released by the dissolution of basaluminite and Na in the solution (0.01 M $NaNO_3$). Adams and Rawajfih (1977) obtained similar precipitates in ageing experiments of basaluminite titrated with NaOH. Prietzel and Hirsch (1998) observed a mixture of basaluminite and alunite after ageing suspensions of $Al_2(SO_4)_3$ solutions titrated with NaOH for 15 weeks and quantifying a mixture of 64% basaluminite and 36% alunite, respectively. Additionally, Nordstrom (1982) concluded that the formation of alunite is due the metastable behaviour of basaluminite.

Combining the presence of basaluminite determined by HEXD (Fig. 4) and the composition of the aqueous phase (Table S2), some insights on the solubility of basaluminite can be extracted. Indeed, after 81 days, the pH changes were almost negligible in all the solutions, and chemical equilibrium was assumed. Similar periods were considered in other solubility studies of aluminium phases (Adams and Rawajfih, 1977; Prietzel and Hirsch, 1998). For the final pH range of 4.61–5.16, basaluminite was confirmed in the solid phase by XRD-HEXD data (Fig. 4), and all major components in the solution were analysed (Table S2). The average Ion Activity Product (IAP) calculated from these 6 analyses was 23.09 ± 0.08. This value is close to 22.3, reported by several researchers for the crystalline material and has been summarized in Nordstrom (1982), and to 24, the value proposed by Singh and

Brydon (1969) and Adams and Rawajfih (1977) for amorphous basaluminite. Moreover, the value is also similar to the value of 23.9 reported by Sánchez-España et al. (2011) for precipitates from pit lakes with a pH range of 4.1–4.8. The existing experimental data for IAP converge towards a narrow window of 22.3–24.0. Nanoboehmite was identified in the solids from the two highest pH values (Fig. 3A). The IAP for the pH value 6.46 (the only one where Al could be analysed) was 9.74 ± 0.02. This value is higher than that reported in the WATEQ4F database for crystalline boehmite ($IAP_{boehmite} = 8.584$), which makes sense due to the nanocrystalline character of the boehmite formed in our experiments.

In parallel to the long ageing experiments, HEXD patterns of synthetic amorphous $Al(OH)_3$ were measured again after one month. The resulting PDF showed an increase in the crystallinity (Fig. 1). This observation supports that not only basaluminite was metastable but also amorphous $Al(OH)_3$, which recrystallized into boehmite.

Comparing the results of both long ageing experiments without and with added sulphate (Fig. 5), for the same amount of OH^- added, the final pH was higher when sulphate was present in solution, and therefore, less OH^- consumption was observed. This effect occurred for all the pH points measured. Consequently, the solids obtained from sulphate-added suspensions were mixtures with a lower percentage of nanoboehmite (Fig. 5D) than those of the solids equilibrated without sulphate. Since there was a high amount of sulphate in solution, the activity of the $AlSO_4^+$ complex was one order of magnitude higher, and therefore, less $Al(OH)_3^0$ complexes were available to precipitate as amorphous $Al(OH)_3$ and subsequently recrystallize to nanoboehmite. Owing to its high concentration in solution, no released sulphate could be calculated. Thus, the presence of dissolved sulphate enhanced the stability of basaluminite, which not only hindered the formation of amorphous $Al(OH)_3$ at higher pH conditions but also retarded its recrystallization to nanoboehmite. This observation is apparently contradictory with that described by Sánchez-España et al. (2016). They report the coexistence of nearly amorphous basaluminite with some nanocrystals (< 100 nm) of $Al(OH)_3$ (gibbsite, bayerite) and allophane formed in the water column of two acid lakes with high sulphate concentration (pH 4.0–4.5, SO_4 = 100–200 mmol/L). However, no proof of ageing of the amorphous basaluminite to crystalline forms of $Al(OH)_3$ and allophane is actually given. Alternatively, some nanocrystals of $Al(OH)_3$ and allophane could also be originally present in what we call basaluminite precipitates, as described by Jones et al. (2011). Further research is needed to clarify this point.

Therefore, the transformation pathway from basaluminite to nanoboehmite includes basaluminite dissolution yielding $Al(OH)_3$ precipitation and its consequent OH^- consumption, resulting in the observed pH decrease. A comparison between the PDFs of pure synthetic basaluminite and amorphous $Al(OH)_3$ reveals an almost identical short-range structure. This fact is surprising and questions the existence of basaluminite as a mineral phase. Indeed, our results suggest that the presence of sulphate does not affect the structure of the amorphous $Al(OH)_3$ matrix. In contrast, our findings point to a stabilisation of amorphous $Al(OH)_3$ via sulphate adsorption. Upon an increase in the solution pH value, the amorphous solid is depleted in sulphate and further hydrolysis of the aluminium results in a crystallization process and the formation of nanoboehmite.

Our results contrast with previous observation from Jones et al. (2011). These authors studied precipitates from sulphate-rich acidic waters using X-ray absorption spectroscopy at the Al, S, and O K-edge. They also observed that both amorphous $Al(OH)_3$ and basaluminite were formed. However, these authors suggested that at pH higher than 7 the solubility of aluminium was controlled by basaluminite. This is in a clear disagreement with our results, which showed that, basaluminite transforms into nanoboehmite with increasing pH, and it was this latter phase which controlled the Al concentration in solution.

Although the influence of pH and sulphate was not systematically studied in the case of schwertmannite, the ageing of basaluminite to nanoboehmite (and natrojarosite) is consistent with that described for schwertmannite transformation to goethite (and jarosite) (Bigham et al., 1996; Acero et al., 2006). The ageing process could have important implications for the trace elements incorporated into basaluminite, whether they are toxic such as As, Se or Mo (Carrero et al., 2017a) or of economic value such as Sc, Y and lanthanides (Ayora et al., 2016), and therefore should be investigated. The instability of basaluminite (and schwertmannite) has to be considered in the use of sludge from AMD treatment to remove phosphorous from municipal and agriculture wastewater effluents (Wei et al., 2008; Sibrell et al., 2009) This process is particularly relevant in the conventional process of P strip and media regeneration by a strong base leaching (Sibrell and Kehler, 2016). Indeed, leaching with a strong base is the conventional procedure to strip the sorbed P and regenerate the sorbing medium (Sibrell and Kehler, 2016). Therefore, the fast transformation of basaluminite to boehmite at high pH would prevent its use as sorbing material for several times.

5. Concluding remarks

Our data support the reinterpretation of basaluminite as an amorphous precipitate. Past studies on the local structure of basaluminite were based on hypotheses that related the structure of basaluminite to that of felsöbanyáite, a rare mineral with the same chemical composition. The results from the PDF analyses show that the local order of both basaluminite and amorphous $Al(OH)_3$ are identical and sulphate is incorporated into the $Al(OH)_3$ structure without any effect on the local structure of the $Al(OH)_3$ precipitate. Owing to Occam's law of parsimony, the demonstrated hypothesis linking the nature of basaluminite to that of an amorphous solid, instead to a rare mineral phase, is therefore preferred.

Basaluminite undergoes several transformations when ageing in aqueous solutions. Considering that synthetic basaluminite has a SO_4:Al ratio higher than the stoichiometry reported in the literature, rather than releasing sorbed sulphate, basaluminite starts to dissolve immediately after its contact with water. The dissolution of basaluminite leads to the precipitation of amorphous $Al(OH)_3$, which, depending on pH and time, a different grade of transformation into boehmite is reached. The experiments demonstrated that basaluminite is a metastable precipitate and that its ageing in/near neutral waters can trigger its transformation into more stable Al hydroxide phases. However, basaluminite tends to stabilize when sulphate is present in solution, inhibiting the formation of $Al(OH)_3$. This process can affect the behaviour of trace elements, both toxic or of economic interest, frequently adsorbed or coprecipitated with basaluminite, and the technological use of this solid phase to remove phosphate from wastewater.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2018.08.002.

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Local structure and ageing of basaluminite at different pH values and sulphate concentrations

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Appendix A. Supplementary data

Contains 3 figures (Figure S1 - S3) and 6 tables (Table S1 – S6)

Figure S1. TGA analysis. Weight loss of pure synthetic basaluminite.

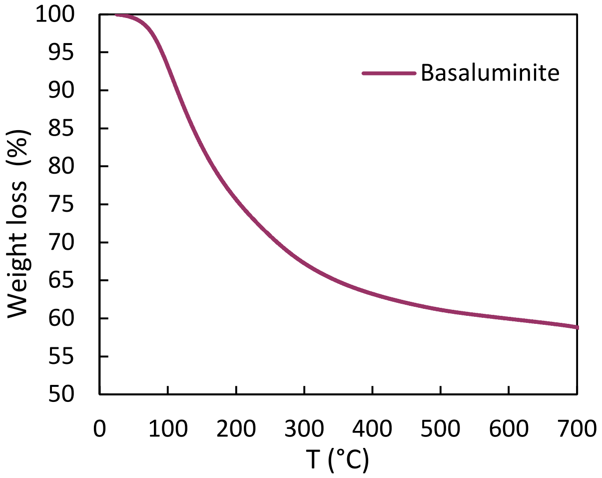

Figure S2. XRD patterns of pure synthetic solids.

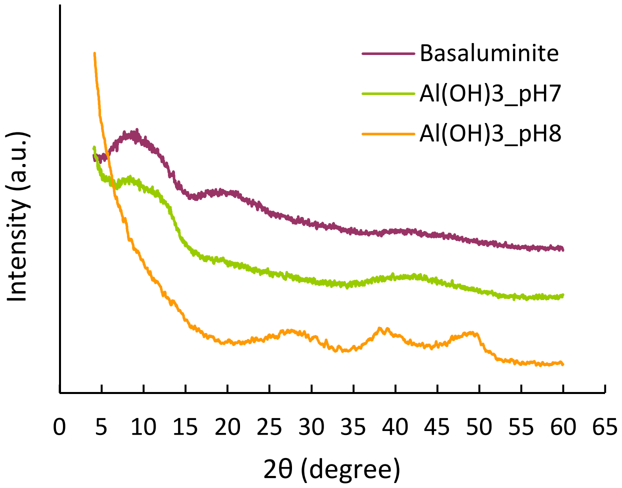

Figure S3. XRD pattern of pure synthetic AlOOH with peaks identified. Boehmite, AlO(OH)-01-083-2384 (C) –Amam (63)-a 3.69360 – b12.21400 – c2.86790- α 90.000 – β 90.000 – γ 90.000.

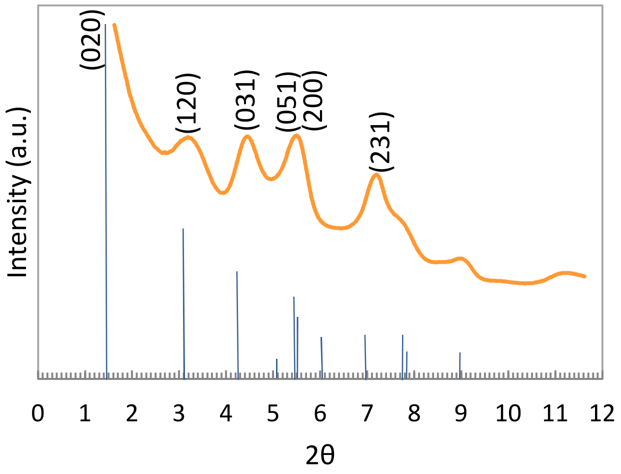

Table S1. Evolution of the aqueous chemistry (mmol/L), percentage of sulfate released from the solid phase and saturation indices for the fast aging experiment. Solid:liquid ratio of 1:1.

Sample	time (h)	pH	Aqueous concentration			% released	Saturation Indices			
			Al	Ca	S	S	Basaluminite	Boehmite	Gibbsite(am)	Gibbsite
B-5min	0.08	4.017	0.005	0.003	0.056	2.14	-6.96	-0.63	-3.66	-1.19
B-10min	0.17	4.016	0.013	0.003	0.068	2.57	-5.32	-0.24	-3.27	-0.80
B-15min	0.25	4.003	0.014	0.003	0.069	2.63	-5.36	-0.26	-3.29	-0.82
B-35min	0.58	4.144	0.044	0.006	0.104	3.96	-2.08	0.60	-2.43	0.04
B-1h	1	4.228	0.065	0.006	0.128	4.88	-0.65	0.99	-2.04	0.42
B-2h	2	4.305	0.126	0.006	0.209	7.95	1.08	1.42	-1.61	0.85
B-6h	6	4.300	0.158	0.007	0.261	9.89	1.34	1.46	-1.57	0.90
B-18h	18	4.336	0.195	0.009	0.318	12.08	1.97	1.62	-1.41	1.06
B-48h	48	4.243	0.219	0.009	0.353	13.42	1.23	1.38	-1.65	0.82
B-96h	96	4.304	0.231	0.009	0.373	14.18	1.88	1.57	-1.46	1.01

Table S2. Aqueous chemistry (mmol/L) at initial and final conditions for the long aging experiment without added sulfate. Solid:liquid ratio of 1:10.

	Initial conditions (48 hours)							Final Conditions (81 days)						
Sample Nº	pH	Al	Na	SO_4	SO_4:Al	% SO_4 released	Added NH_4OH 0.5 M (µL)	pH	Al	Na	SO_4	mmol SO_4 released	% SO_4 released	mmol excess OH
1	**4.95**	0.040	10.135	0.073	1.82	23.81	0	**4.61**	0.055	9.030	0.080	0.000	3.97	0.000
2	**4.95**	0.044	9.978	0.077	1.76	22.72	10	**4.75**	0.035	8.946	0.088	0.001	4.76	0.005
3	**4.98**	0.043	10.161	0.076	1.79	23.50	15	**4.81**	0.023	9.070	0.088	0.001	5.96	0.007
4	**4.98**	0.043	10.061	0.077	1.80	23.89	20	**4.91**	0.014	9.071	0.088	0.001	5.71	0.010
5	**4.98**	0.042	10.230	0.077	1.80	23.85	25	**5.10**	0.005	9.016	0.095	0.001	9.38	0.012
6	**4.99**	0.043	10.099	0.077	1.78	22.15	30	**5.16**	0.004	8.897	0.105	0.001	12.44	0.015
7	**4.98**	0.042	10.010	0.075	1.81	23.49	40	**5.44**	0.001	8.947	0.116	0.002	20.37	0.020
8	**4.98**	0.043	10.002	0.076	1.77	22.92	50	**5.46**	≤ D.L.	8.986	0.146	0.004	33.64	0.025
9	**4.99**	0.040	9.877	0.070	1.77	22.91	60	**5.47**	≤ D.L.	8.841	0.173	0.005	53.34	0.030
10	**4.99**	0.040	10.004	0.073	1.81	23.08	70	**5.55**	≤ D.L.	8.878	0.200	0.006	64.25	0.035
11	**4.99**	0.041	9.938	0.071	1.75	22.96	80	**5.85**	≤ D.L.	8.816	0.219	0.007	75.86	0.040
12	**4.99**	0.039	9.854	0.071	1.83	23.08	100	**6.46**	0.001	8.688	0.236	0.008	83.25	0.050

Table S3. Saturation indices at initial and final conditions for the long aging experiment without added sulfate.

Initial conditions (48 hours)						Final conditions (81 hours)					
pH	Basaluminite	$Al(OH)_3$(a)	Gibbsite	Boehmite	Alunite(Na)	pH	Basaluminite	$Al(OH)_3$(a)	Gibbsite	Boehmite	Alunite(Na)
4.89	2.47	-0.96	1.73	1.26	1.71	**4.61**	0.29	-1.68	1.01	0.53	0.59
4.93	2.66	-0.92	1.77	1.30	1.88	**4.74**	0.78	-1.50	1.19	0.71	0.80
4.97	2.83	-0.86	1.83	1.36	1.96	**4.77**	0.54	-1.54	1.15	0.68	0.54
4.95	2.84	-0.86	1.83	1.36	1.97	**4.86**	0.45	-1.51	1.18	0.71	0.33
4.98	2.79	-0.87	1.82	1.35	1.94	**5.12**	0.10	-1.51	1.18	0.71	-0.17
4.99	2.91	-0.83	1.86	1.38	2.01	**5.17**	0.14	-1.48	1.21	0.74	-0.18
4.99	2.79	-0.87	1.82	1.35	1.92	**5.44**	-1.00	-1.62	1.07	0.60	-1.46
4.98	2.84	-0.86	1.83	1.36	1.96	**5.43**	-1.50	-1.77	0.92	0.44	-1.68
4.99	2.76	-0.86	1.83	1.35	1.84	**5.47**	-4.86	-2.67	0.02	-0.45	-4.01
4.99	2.77	-0.86	1.83	1.35	1.88	**5.51**	-2.21	-1.94	0.75	0.27	-2.18
4.98	2.81	-0.85	1.84	1.36	1.89	**5.87**	-1.32	-1.58	1.11	0.64	-1.92
4.97	2.72	-0.87	1.82	1.34	1.82	**6.37**	-0.43	-1.06	1.63	1.16	-2.13

Table S4: Evolution of pH values for slow aging experiments.

		Without SO_4					With SO_4				
	µL 0.5M NH_4OH	0h	40h	19d	39d	81d	0h	40h	19d	39d	81d
1	0	4.95	4.48	4.56	4.62	4.61	5.08	5.75	5.13	5.13	5.06
2	10	5.20	4.59	4.70	4.75	4.75	6.00	5.35	5.33	5.27	5.20
3	15	5.38	4.70	4.81	4.84	4.81	7.06	5.66	5.51	5.51	5.38
4	20	5.86	4.84	4.91	4.93	4.91	7.09	5.89	5.70	5.57	5.52
5	25	7.19	5.16	5.24	5.23	5.10	7.09	6.34	6.06	5.93	5.74
6	30	7.72	5.25	5.32	5.30	5.16	6.62	6.50	6.16	6.10	5.84
7	40	8.21	5.70	5.78	5.72	5.44	6.60	7.24	6.68	6.53	6.27
8	50	8.64	6.15	6.11	5.80	5.46	6.04	7.76	6.97	6.67	6.33
9	60	8.93	7.13	6.25	5.80	5.47	6.08	8.30	7.37	6.85	6.43
10	70	9.00	7.64	6.31	6.01	5.55	6.12	8.36	7.67	7.06	6.50
11	80	9.10	7.86	6.46	6.26	5.85	6.14	8.58	8.24	7.69	6.56
12	100	9.22	8.29	7.75	6.79	6.46	6.16	8.70	8.82	8.62	7.18

Table S5. Aqueous chemistry (mmol/L) at initial and final conditions for the long aging experiment with sulfate added (18.73 mmol/L). Solid:liquid ratio of 1:10.

	Initial conditions (48 hours)				added	Final Conditions (81 days)			
	pH	Al	Na	SO_4	NH_4OH 0.5 M (µL)	pH	Al	Na	SO_4
1	**5.08**	-	-	-	0	**5.06**	0.02	49.053	20.827
2	**5.11**	-	-	-	10	**5.20**	≤ D.L.	49.123	20.806
3	**5.11**	0.012	48.818	21.456	15	**5.38**	≤ D.L.	47.226	20.378
4	**5.13**	0.013	50.057	21.191	20	**5.52**	≤ D.L.	48.060	20.966
5	**5.13**	0.012	46.314	20.526	25	**5.74**	≤ D.L.	49.065	21.401
6	**5.12**	0.015	49.561	20.891	30	**5.84**	≤ D.L.	47.284	20.245
7	**5.12**	0.013	48.685	21.184	40	**6.27**	≤ D.L.	46.006	20.701
8	**5.13**	0.012	48.432	21.042	50	**6.33**	≤ D.L.	47.296	21.089
9	**5.14**	0.013	48.480	21.362	60	**6.43**	≤ D.L.	49.135	21.139
10	**5.10**	0.012	49.542	21.251	70	**6.50**	≤ D.L.	49.952	21.695
11	**5.13**	0.012	49.745	21.165	80	**6.56**	≤ D.L.	50.303	21.756
12	**5.12**	0.011	50.904	21.566	100	**7.18**	≤ D.L.	49.094	21.335

Table S6. Saturation indices at initial and final conditions for the long aging experiment with sulfate added.

Initial conditions (48 hours)						Final conditions (81 hours)					
pH	Basaluminite	$Al(OH)_3(a)$	Gibbsite	Boehmite	Alunite(Na)	pH	Basaluminite	$Al(OH)_3(a)$	Gibbsite	Boehmite	Alunite(Na)
5.11	-0.25	-2.11	0.58	0.10	2.82	**5.06**	0.18	-2.03	0.66	0.19	3.20
5.13	0.08	-2.02	0.67	0.20	3.05	**5.20**	-1.09	-2.28	0.41	-0.06	2.04
5.13	-0.02	-2.05	0.64	0.17	2.93	**5.38**	-7.18	-3.71	-1.02	-1.49	-2.82
5.12	0.26	-1.98	0.71	0.24	3.18	**5.52**	-0.97	-2.08	0.61	0.13	1.65
5.12	-0.03	-2.05	0.64	0.16	2.97	**5.74**	0.59	-1.59	1.10	0.63	2.51
5.13	-0.15	-2.08	0.61	0.14	2.86	**5.84**	1.21	-1.38	1.31	0.84	2.79
5.14	0.06	-2.02	0.67	0.19	3.01	**6.27**	2.16	-0.93	1.76	1.29	2.85
5.10	-0.27	-2.12	0.57	0.09	2.81	**6.33**	2.09	-0.92	1.77	1.30	2.72
5.13	0.04	-2.03	0.66	0.19	3.00	**6.43**	1.85	-0.92	1.77	1.29	2.41
5.12	-0.33	-2.13	0.56	0.09	2.76	**6.50**	1.67	-0.94	1.75	1.28	2.19
5.13	-0.02	-2.05	0.64	0.17	2.96	**6.56**	1.43	-0.97	1.72	1.25	1.92
5.12	0.05	-2.03	0.66	0.18	3.04	**7.18**	-1.77	-1.46	1.23	0.76	-1.43

Article 2

Sorption of rare earth elements onto basaluminite: The role of sulfate and pH

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Sorption of rare earth elements onto basaluminite: The role of sulfate and pH

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Abstract

Scandium, yttrium and lanthanides (REE) are critical raw materials in increasing demand for modern technology, so identifying and developing new sources of REE has become a pressing need. REE concentrations in acid mine drainage (AMD) are several orders of magnitude higher than those in natural water, and their recovery is of economic interest. Passive remediation systems designed to minimize AMD impact on the ecosystem retain REE in solid waste, where basaluminite, $Al_4SO_4(OH)_{10}\cdot 5H_2O$, is the mineral responsible for the scavenge. However, no information about the retention mechanisms of REE is currently available in the literature. The objective of the present work is to study the adsorption of lanthanides, yttrium and scandium onto synthetic basaluminite over a pH range of 4–7 at room conditions. Since sulfate is ubiquitous in AMD, the adsorption has been investigated with variable sulfate concentrations.

Experimental results show that sorption onto basaluminite is strongly dependent on pH, starting at pH 5 for lanthanides and yttrium and at pH 4 for scandium. At any given pH values, sorption increases with sulfate concentration. Distribution coefficients, defined as $K_D = [REE_{sorbed}]/[REE_{solution}]$, are higher for Sc, and across the lanthanide series, the distribution coefficients increase from La to Lu according to decreasing ionic radius, where yttrium is considered close to Ho. Experimental results were modeled using a sorption model that considers mass law equations where the strong sulfate aqueous complex, MSO_4^+, is adsorbed by exchanging a proton with the mineral surface. The dependence of the experimental results on pH suggests the formation of monodentate binding for Y and lanthanides. The bidentate complex for Sc is deduced by the two proton exchange per mol of Sc extracted from the experiments. The thermodynamic constants for the surface complexation reactions were obtained from experiments with high sulfate concentration and were successfully applied to the experiment with low sulfate content and different solid-liquid ratios. Therefore, the model can be applied to interpret the REE geochemistry in natural systems with variable pH and sulfate concentrations.

Keywords: Sorption model; Scandium; Yttrium; Lanthanides; Fractionation; Sorption edge; Non-electrostatic model; Monodentate surface species

1. INTRODUCTION

In the last two decades, there has been an increasing interest in REE, referred to here as the lanthanide series plus yttrium and scandium, due to their high demand in modern industries. The low supply is due to limited REE

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mining to find new sources of REE (Alonso et al., 2012; Hatch, 2012). Moreover, as a consequence of this industrial activity, new potential pollution sources of REE in natural waters have also emerged (Pagano et al., 2015; Isildar et al., 2018).

Noack et al. (2014) presented a comprehensive study of the REE distribution in groundwater, lakes, rivers and oceans. In particular, REE concentrations in acid mine drainage (AMD) are several orders of magnitude more abundant than other natural water. From the forensic point of view, the REE distribution pattern normalized to the North American Shale Composite (NASC), has been used to prove the impact of Acid Mine Drainage (AMD) in groundwater, rivers and estuarine environments (Delgado et al., 2012; Grawunder et al., 2014; Morgan et al., 2016; Bonnail et al., 2017; Li and Wu, 2017). It is generally recognized that the REE concentration in water is largely controlled by solid surface and aqueous solution chemistry (Quinn et al., 2006a,b and references therein).

REE fractionation between minerals and AMD has been studied since the early 1990s as rock weathering (Auqué et al., 1993, Gimeno et al., 1996) and in mining areas (Gammons et al., 2003). Verplanck et al. (2004) observed REE scavenging from AMD by hydrous ferric oxides as the pH increased to 5.1 due to the water mixing. Similar results were observed by Gammons et al. (2005a,b) when volcanic acidic water mixed with a tributary with neutral pH and the pH increased from 4.3 to 6.1, and when an acidic creek was mixed with a tributary river with circumneutral pH. There, mixtures of ferric and aluminum secondary precipitates were described as being responsible for REE scavenging, yielding Heavy REE (HREE) enrichment in the solids. Similar observations were made by Ferreira da Silva et al. (2009) in the AMD of the Lousal Mine (S. Portugal), where a decrease in REE concentrations was observed as the pH increased from 3 to 6 due to the confluence with a tributary stream. All the aforementioned studies suggested sorption mechanisms on Fe and Al hydroxysulfates as responsible for REE retention. Therefore, interaction with the most relevant solids formed in AMD environments, schwertmannite ($Fe_8O_8(OH)_6SO_4$) and basaluminite ($Al_4SO_4(OH)_{10}\cdot 5H_2O$), is expected to play a relevant role in the characteristic water lanthanide distribution pattern.

On the other hand, the treatment of AMD in neutralization plants results in a high amount of sludge made up of schwertmannite and basaluminite. Due to its high water content, the disposal and storage of this waste represents a major operating cost and environmental concern for coal and metal mining operations (Ackman, 1982; Viadero et al., 2006). Similarly, passive mediation systems neutralize AMD by intercepting its natural flux with a permeable filter of limestone (Caraballo et al., 2011). Along this process, sequential precipitation of schwertmannite and basaluminite occurs, causing two well differentiated layers of the solids. Basaluminite retains Sc, Y and lanthanides in the system when it forms at pH values from 4.5 to 6 (Ayora et al., 2016). The REE concentration in basaluminite ranges from 2 to 12 μmol/g, depending on the REE values in the input, and these concentrations are comparable to the grades found in REE deposits and exploration targets (Berger et al., 2009). Despite the fact that schwertmannite precipitates before basaluminite (from pH 3–3.5), it does not retain REE. Therefore, a detailed understanding of the mechanism responsible for selective REE scavenging is necessary.

Currently, most REE sorption and fractionation studies have focused on hydrous ferric and manganese oxides in marine water (Byrne and Kim, 1990; Bau et al., 1996) and interactions between synthetic marine water and manganese and ferric oxides (Koeppenkastrop and De Carlo, 1992; Pourret and Davranche, 2013). Differences in solid origin and water source result in distinct fractionation. Light REE (LREE) enrichments were observed in silica phases (Byrne and Kim 1990) as well as in synthetic MnO_2 and α-FeOOH solids (Koeppenkastrop and De Carlo, 1992). In contrast, HREE enrichment was observed in synthetic FeOOH and MnO_2 (De Carlo et al., 1998) as well as hydrogenetic Mn-Fe crusts (Bau et al., 1996). With application to continental water, Liu et al. (2017) developed a surface complexation model (SCM) to interpret REE sorption in iron hydroxide. Additionally, other studies focused on REE interaction with organic matter and its affection with the organic acids of soils (Tang and Johannesson 2003; Verplanck et al., 2004; Pourret and Martinez, 2009).

Aluminum phases are not as common as ferrous oxide phases, and there are few studies related to the REE uptake for aluminum oxides. For example, the uptake of Eu and Yb by alumina (Al_2O_3), at varying pH, ionic strength and acid fulvic concentrations, has been studied by soil scientists as an analogue for actinides in nuclear waste disposal (Xiangke et al., 2000). Experimental sorption edges for Yb and Eu(III) onto alumina were reproduced by Marmier et al. (1997) and Rabung et al. (2000), respectively, using an SCM. In all of the studies, the REE sorption is dependent on pH.

In addition to pH, sulfate has the potential to change the sorption behavior of REE and other metals in AMD systems. Indeed, aqueous sulfate complexes are predominant in AMD over a wide range of pH values (Gimeno et al., 2000), and sulfate is a major constituent of the Fe and Al solid phases, schwertmannite and basaluminite. Therefore, sulfate is expected to play a major role in aqueous-solid partitioning. Despite their key role in AMD geochemistry, no experimental or modeling studies of REE sorption for these two minerals have been investigated. In this study, we present experimental results for adsorption of REE onto synthetic basaluminite as a function of pH and two different sulfate concentrations. To understand the REE sorption mechanism onto basaluminite, a surface complexation model is proposed from a sorption experiment with sulfate and subsequently validated with a second experiment at very low sulfate concentration.

2. MATERIALS AND METHODS

2.1. Experimental part

2.1.1. *Preparation and characterization of synthetic basaluminite*

Basaluminite was synthesized following the method described by Adams and Rawajfih (1977) by adding

214 mL of 0.015 M $Ca(OH)_2$ to 30 mL of 0.05 M $Al_2(SO_4)_3 \cdot 18H_2O$; both commercial reagents. The resulting solid was washed several times with Milli-Q water to remove the coprecipitated gypsum, and dried for 2 days at 40 °C. As shown by X-ray diffraction (XRD), the resulting solid was free of impurities (Fig. SI-1).

The specific surface area was obtained by the BET-N_2 sorption method, using a Micromeritics Gemini V analyzer˙ The sorption site density was calculated based from the crystal structure of felsöbanyáite, with a local order similar to that of basaluminite (Farkas and Pertlik, 1997; Carrero et al., 2017).

2.1.2. *REE sorption as function of pH and sulfate*

Two sets of batch experiments were performed to study the SO_4 dependence of REE adsorption onto synthetic basaluminite as a function of pH: low and high sulfate concentration. Two stock solutions were prepared from an ICP standard mix (Merck) of 16 elements –excluding Pm- with Milli-Q water (the total REE in the stock solution was 123.3 µM). The first stock solution consisted of 1 mg/L of each REE, whereas the second stock solution contained 1 mg/L of each REE plus 20 mg/L Na_2SO_4. The initial pH of the stock solutions was 2.5. A sequence of 10 mL aliquots of each stock solution were adjusted to a desired pH range of 4.5–7 via addition of a 0.05 M NH_4OH solution. The first set of experiments was carried out by adding 10 mg of synthetic basaluminite to each aliquot of the first stock solution. Despite aqueous sulfate is initially absent, this set of experiments will hereafter be referred to as a low sulfate (0.5 mM SO_4) due to the release of small amounts of sulfate adsorbed in the synthesis of basaluminite (see chapter 3.2). The second set of experiments was similar to the first one, but using the second stock solution (20 mM SO_4). Finally, a third set of batch experiments with a different solid:liquid ratio was performed to test the validity of the model developed. It consisted of suspensions of 10 mg of synthetic basaluminite in 40 mL of the second stock solution (20 mM SO_4).

The solid was added to each solution and the suspensions were shaken for 6 hours at room temperature. Previous kinetic experiments were performed at pH 6–6.5, and maximum adsorption was reached at 6 hours and continued from there on. Similar results were obtained by Koeppenksastrop and De Carlo (1992) with fast REE adsorption onto MnO_2, hydroxyapatite and goethite and amorphous FeOOH, reaching an uptake of 60–90% of the initial dissolved REE in 4 hours. Due to basaluminite instability (Lozano et al., 2018), equilibrium times longer than 6 hours were not used. Each pH was readjusted to the initial value after basaluminite addition because the pH drops when the mineral exchanges SO_4 with OH. Once the experiment finished, the suspensions were centrifuged for 15 min at 4500 rpm (4150 RCF). The supernatant was filtered through 0.22 µm nylon membranes into test tubes. The filtered supernatant samples were diluted fivefold with 1% HNO_3. The REE concentrations in the solutions were determined by ICP-MS. Raw data from each experiment were corrected by a dilution factor based on the amount of NH_4OH added. The solids were dried at 40 °C for 48 h. The reproducibility of the experiments was determined by replication at pH 6.7. The error of the final pH values was ±0.02. The sorbed fractions were calculated as follows:

$$\text{Sorbed fraction} = \frac{[\text{REE}]_{\text{initial}} - [\text{REE}]_{\text{final}}}{[\text{REE}]_{\text{initial}}} \qquad (1)$$

where [REE] is the concentration of each REE. Initial concentration was measured from stock solution and final concentration in each different batch after experiment. The distribution coefficients K_D (L/kg) were calculated from the REE sorbed onto the solid per the concentration of REE remained in solution and normalized per volume of solution and mass of solid (solid to liquid ratio):

$$K_D = \frac{[\text{REE}]_{\text{initial}} - [\text{REE}]_{\text{final}}}{[\text{REE}]_{\text{final}}} \cdot \frac{V_{\text{solution}}}{M_{\text{solid}}} \qquad (2)$$

2.1.3. *Analytical techniques*

Measurements of pH values from filtered aliquots were made with a Crison® glass electrode calibrated with buffer solutions of pH 2, 4, 7 and 9. Major cation (S, Al, and Na) concentrations were measured by ICP-AES (Thermo Scientific – iCAP 6500, Radial acquisition) and REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y and Sc) were determined with ICP-MS (Perkin-Elmer®SciexElan 6000). The detection limits were 1.6, 1.0 and 4.3 µmol/L for S, Al and Na, respectively, and 0.2 µg/L for REE. The analytical precision error was estimated to be approximately 5% for ICP-AES and 2% for ICP-MS measurements. Certified solutions (CPI International-CCV standard 1-solution A) and two AMD laboratory standards supplied by P. Verplanck (USGS), were intercalated within the samples to check the analytical accuracy. The deviation from the recommended values was always lower than 5%, with the exception of Eu, giving values 20% below the value reported by Verplanck et al. (2001).

The solid phase prior and after the sorption experiments was investigated by High Energy X-ray Diffraction (HEXD) at the ID31 beamline at the European Synchrotron Radiation Facility (ESRF).

2.2. REE speciation

Chemical speciation of dissolved REE and surface complexation modeling was calculated by PHREEQC code (Parkhurst and Appelo, 1999) using the database of Donnee Thermoddem_V1.10 (Blanc et al., 2012). The database has been updated with the stability constants at zero ionic strength and 25 °C for the following inorganic complexes for lanthanides and yttrium (M): MCO_3^+, $M(CO_3)_2^-$ and $MHCO_3^{2+}$ (Luo and Byrne, 2004); MSO_4^+ (Schijf and Byrne, 2004); MOH^{2+} (Klungness and Byrne, 2000), $M(OH)_2^+$, $M(OH)_3^0$ (Lee and Byrne, 1992); MCl^{2+} (Luo and Byrne, 2001); MF^{2+}, MF_2^+ (Luo and Millero, 2004); and MNO_3^{2+} (Millero, 1992). Solubility products for REE solids, $M(OH)_3$ and $M(OH)_3(am)$, were added from LLNL database (Johnson et al., 2000) database and Spahiu and Bruno (1995). Scandium aqueous complexes, $Sc(OH)^{2+}$,

$Sc(OH)_2^+$, $Sc(OH)_3^0$, $ScSO_4^+$; and the solubility product for $Sc(OH)_3$ by Wood and Samson (2006) were also added to Donnee Thermoddem_V1.10 database. Equilibrium constants for aqueous species are compiled in Table SI-1 of Supporting Information.

3. RESULTS

3.1. Basaluminite characterization

The BET method measured a specific surface area of 68 m^2/g. The potentiometric titrations of synthetic basaluminite have been attempted at three different ionic strengths, 0.1, 0.02 and 0.005 M of $NaNO_3$. However, the mineral is proved to release sulfate and transform into nanoboehmite as OH^- is incorporated to the solution (Lozano et al., 2018). This behavior prevented the acquisition of consistent titration curves and their prediction with current electrostatic models. Therefore, the surface properties could not be obtained. Then, the site densities were calculated from crystal structure of felsőbányaite, as basaluminite presents similar local order, as stated by Farkas and Pertlik (1997) and Carrero et al. (2017). The single coordinate sites (one oxygen atom linked to one Al atom) calculated were 4.94, 4.24 and 4.70 nm^{-2} for the 100, 010 and 001 faces, respectively, (5.5 sites/112.32 $Å^2$ for (100), 6.25/147.38^2 for (010) and 6.25/132.80^2 for (001)) from the unit cell of basaluminite, with a space group of P_21. The average surface site is 4.60 nm^{-2} (see Fig. SI-2 for structural details).

3.2. REE adsorption as a function of pH and sulfate

The chemical compositions of the initial and final solutions of the two sets of experiments with 1 g/L of solid:liquid ratio are compiled in Table SI-2. All final solutions were subsaturated with respect to the REE hydroxides (Table SI-3), and, therefore, no REE hydroxide precipitation was expected. All the final solutions except one were supersaturated with respect to basaluminite (Saturation indices between 0.06 and 1.3).

Small amounts of dissolved sulfate were present in the final solutions without initial sulfate. There, the amount of dissolved sulfate increased from 0.1 to 0.9 mM with increasing pH. This is interpreted as the exchange of sulfate from basaluminite with OH groups from the solution (Lozano et al., 2018). The experiments without initial sulfate will be hereafter noted as 0.5 mM SO_4, indicating the mean value.

Four elements were selected for representation: La as light REE (LREE), Lu as heavy REE (HREE), Sc and Y. The two sets of sorption experiments with different sulfate concentrations showed increasing REE sorption with pH (Fig. 1). The adsorption edges occur over a range of 2.0 to 2.5 pH units. Lanthanides and yttrium sorption became significant at pH 5. However, the pH values at which different REE are sorbed differ for each element. The sorption edges shifted to lower pH values for HREE with respect to LREE, and preferential sorption of HREE over LREE was observed. Scandium behaved differently, being scavenged at pH values considerably lower than the rest, and sorption of Sc became significant at pH 4. Similar pH dependence was observed in the experiment with 0.25 g/L of solid:liquid ratio. As expected, the sorption edges are shifter to higher pH values (Table SI-4), as it will be commented in Section 4.3.

The sulfate dependence of REE sorption is more evident by plotting the results of both experiments together by element (Fig. 2). REE sorption is greater when sulfate is present in solution along the entire pH range studied. Sorption enhancement varies with the pH range for each element. For instance, at pH 5.4 the sorption fraction for the higher sulfate in solution is 0.2 points higher for Lu, 0.1 points for Y, 0.1 for Sc and 0.05 for La. This enhancement increases at pH 6: for Lu (0.3 points higher) and for Y (0.2 points) but decreases for Sc (0.05) and for La, which has the same sorbed fraction. The effect for the enhancement of REE sorption with higher sulfate concentration has also been

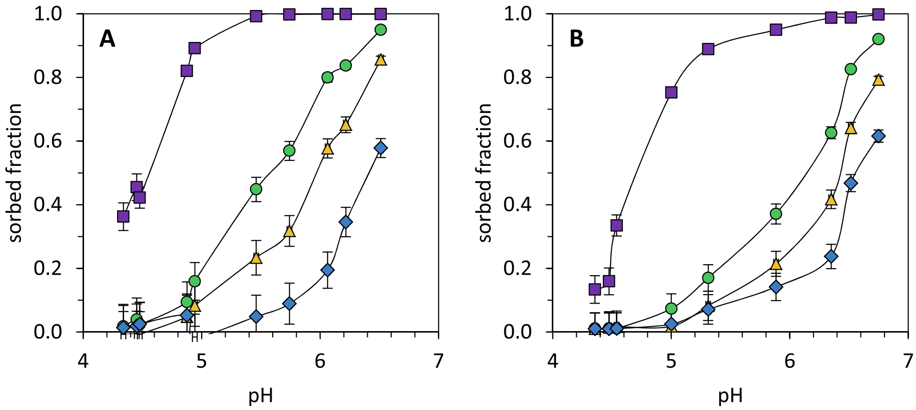

Fig. 1. Sorption edges of (A) sorption with 20 mM of sulfate, (B) sorption with 0.5 mM of sulfate in solution. (Sc: squares, Y: triangles, Lu: circles and La: diamonds). Uncertainties in pH measurements and in the sorbed fraction are considered as ±0.02 and from ±0.01 to ±0.08, respectively, indicated by error bars.

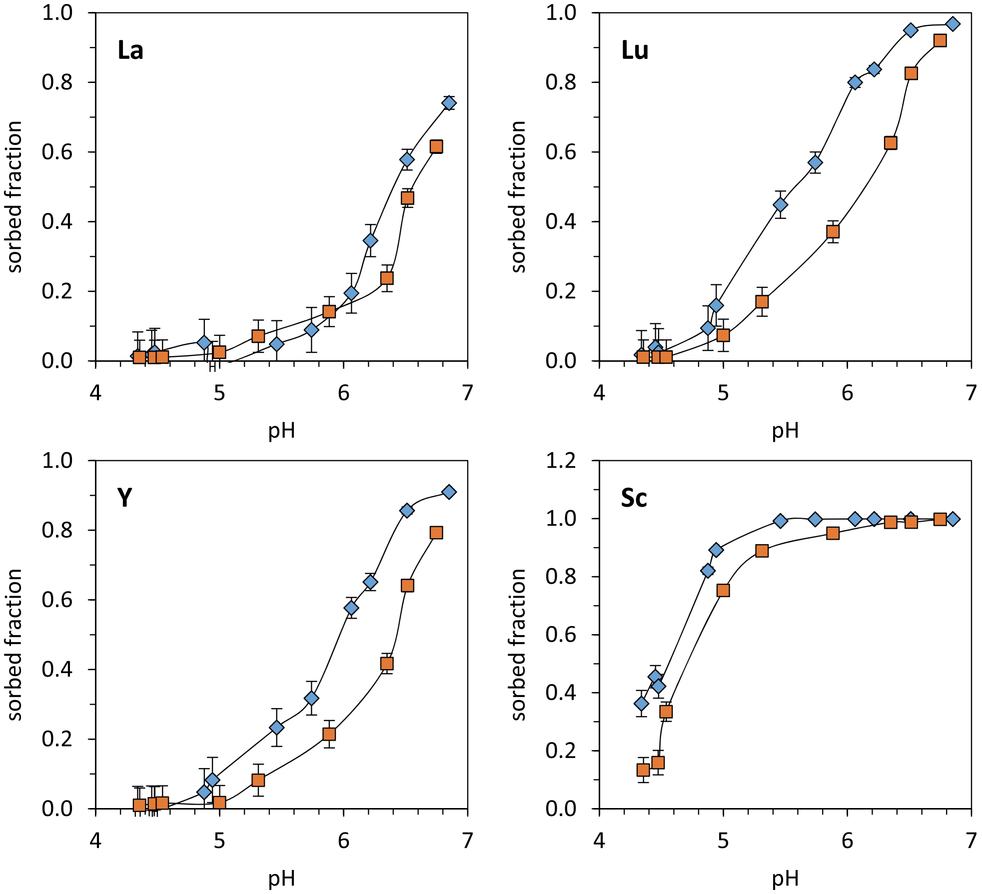

Fig. 2. Comparison of REE sorbed fraction dependence on sulfate concentration for four selected elements. Sorption with 0.5 mM SO_4 in red squares and sorption with 20 mM SO_4 in blue diamonds.

observed for other trace metal sorption, such as Cu and Pb, onto ferrihydrite and schwertmannite (Webster et al., 1998; Baleeiro et al., 2018). Webster et al. (1998) concluded that the enhanced sorption of Cu onto iron (III) oxy-hydroxy sulfate observed with higher sulfate in solution was due to the formation of ternary complexes with a ferric surface site, e.g., $\equiv FeOHCuSO_4$. Similarly, Baleeiro et al. (2018) pointed out that these kinds of ternary surface complexes could explain the strong affinity of these trace metals with schwertmannite.

Values for the distribution coefficient (K_D) were calculated by Eq. (2) and are presented for the lanthanide series in Fig. 3. At pH values lower than 5, the distribution patterns are almost flat and from pH 5 upwards, when the sorbed fraction is significant, log K_D patterns reflect HREE enrichment relative to LREE in the solid phase (Fig. 3), varying 1 unit of log K_D along the series in both sets of experiments. Similar patterns were observed by Bau 1999 for their coprecipitation experiments of REE and Fe at low pH values. Similar relative enrichment in heavy lanthanides was observed in aluminum and ferric hydroxides precipitated in acidic rivers after their neutralization via mixing with alkaline tributaries (Gammons et al. 2003, 2005; Verplanck et al., 2004). Similar to those described by Masuda et al. (1987) and Bau (1996), the fractionation patterns showed an M-type tetrad effect (where they can be subdivided into four convex segments: from La to Nd, from Nd to Gd, from Gd to Ho and from Ho to Lu (Fig. 3). A small positive Ce anomaly was observed only at low pH and low SO_4 concentration, possibly due to a partial/total oxidation of Ce^{3+} to Ce^{4+}, as Koeppenkastrop and De Carlo (1992) proposed for the positive anomalies observed in vernadite. Yttrium has a similar ionic radius as Dy and Ho and can be placed between them (not shown in the figure). For the different pH values represented in Fig. 3, the log K_D patterns show a negative Y anomaly. This anomaly is expressed in K_D^Y/K_D^{Dy} and K_D^Y/K_D^{Ho} ratios below unity, which is observed along the pH range for both sets of experiments with 20 and 0.5 mM sulfate concentration (Table SI-5). In the experiments with low SO_4 concentration, Yb and Dy displayed negative anomalies that attenuated as the pH increased. These anomalies were absent at high sulfate concentrations. In contrast, at higher sulfate concentrations, Er showed a negative anomaly at lower pH values that was attenuated when pH increased and this Er anomaly was not observed with lower sulfate content. These anomalies are not previously described in similar sorption/coprecipitation

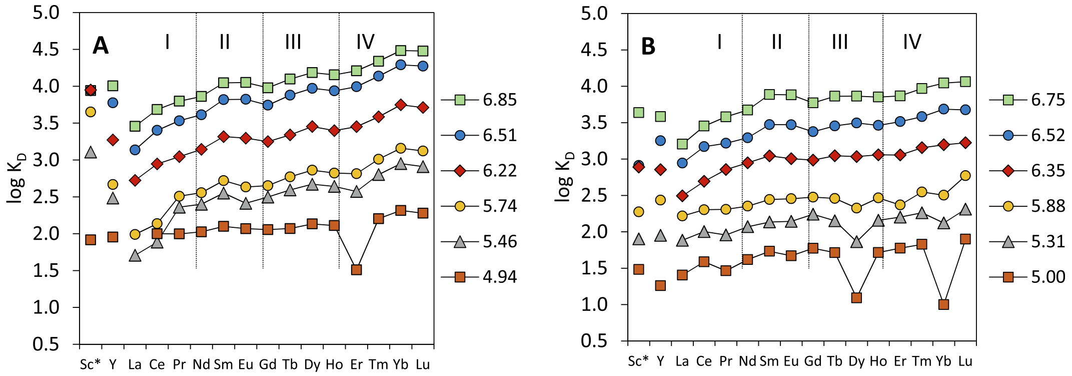

Fig. 3. Patterns of log K_D values showing lanthanide M-type tetrad effect. (A) solution with 20 mM SO_4; (B) solution with 0.5 mM SO_4. (log $K_D^{Sc*} = \log K_D^{Sc} - 2$).

experiments using amorphous ferric hydroxides (Bau, 1999; Ohta and Kawabe, 2000; Quinn et al., 2006a).

4. DISCUSSION

4.1. Aqueous speciation

The presence of sulfate in the solution affects the REE aqueous speciation since it strongly complexes with REE (Gimeno et al., 2000). The proportion of sulfate complexes increases with sulfate concentration and becomes predominant for SO_4 concentrations higher than 1 mM. The rest of the aqueous complexes, MOH^{2+}, MCO_3^+ and $M(CO_3)_2^-$ are only significant at pH values higher than 6.5 and low SO_4 concentrations, as represented for Y in Fig. 4A, B and extended for the rest of lanthanides. Scandium speciation differs from the rest, where Sc hydrolysis complexes are also significant at pH values higher than 4.6 (Fig. 4C, D). For Sc, there is no information about the carbonate complexation in the literature (Wood and Samson 2006), possibly because $ScCO_3^+$ formation is not thermodynamically favorable compared to the formation of strong hydrolysis products.

4.2. Model description

Surface Complexation Models (SCM) are commonly referred to as providing chemical and molecular descriptions of adsorption using equilibrium thermodynamics that can be applied to different conditions (Goldberg, 1992). The common characteristics of these models are the surface charge balance, electrostatic potential terms, as an effect of surface charge, and several adjustable parameters: equilibrium constants, total number of reactive sites and capacitance density.

In a non-electrostatic model (NEM), the electrostatic term is ruled out when the chemical interaction of the cations adsorption is stronger than electrostatic forces in the sorption process (Davis and Kent, 1990). For REE in particular, several works model the sorption experimental data with NEM, and thus, discard the electrostatic term. Marmier and Fromage (1999) reported a non-electrostatic surface complexation model to describe the sorption of lanthanum in hematite. Tertre et al. (2008) described a non-electrostatic model for REE adsorption on basaltic rock. Rabung et al., (2000) and Quinn et al., (2006a,b) also described a sorption model for Y and lanthanides in amorphous iron hydroxides without taking into account the electrostatic term. In our case, the metaestable character of the mineral precluded the full determination of basaluminite surface properties and thus, a non-electrostatic model will be used.

On the other hand, models proposed for REE sorption on amorphous ferric and manganese oxides, hematite, goethite, aluminum hydroxide and alumina are traditionally explained by the sorption of free ions onto surface sites (Tochiyama et al., 1996, Rabung et al., 1998; Marmier et al., 1997; Marmier and Fromage 1999; Quinn et al., 2006a). In the present work, owing to the predominance of sulfate complexes in the aqueous phase, the experiments were initially modeled by the reaction of the aqueous sulfate complex MSO_4^+ with surface sites. This result is consistent with the observation of higher adsorption in the experiments with the SO_4-rich solutions (20 mM). In the case of Sc, in addition to $ScSO_4^+$, the aqueous speciation showed a higher stability of the hydrolysis species $Sc(OH)^{2+}$ in the experiments with lower sulfate concentration (Fig. 4C, D), and the sorption of this aqueous species was also considered. Although experiments were conducted at room conditions, carbonate complexation has not been considered experimentally since the proportion of carbonate species is very low at the experimental pH range (Fig. 4).

The sorption reaction is proposed as the exchange of the M^{z+} aqueous complex (M^{z+} accounting for MSO_4^+ and $Sc(OH)^{2+}$) with n protons from n surface sites represented by XOH:

$$M^{z+} + nXOH = (XO)_n M^{z-n} + nH^+ \qquad K_M \tag{3}$$

The equilibrium constant K_M of the reaction for each REE (M) would be:

$$K_M = \frac{\{(XO)_n M^{z-n}\} \cdot a_{H^+}^n}{a_{M^{z+}} \{XOH\}^n} \tag{4}$$

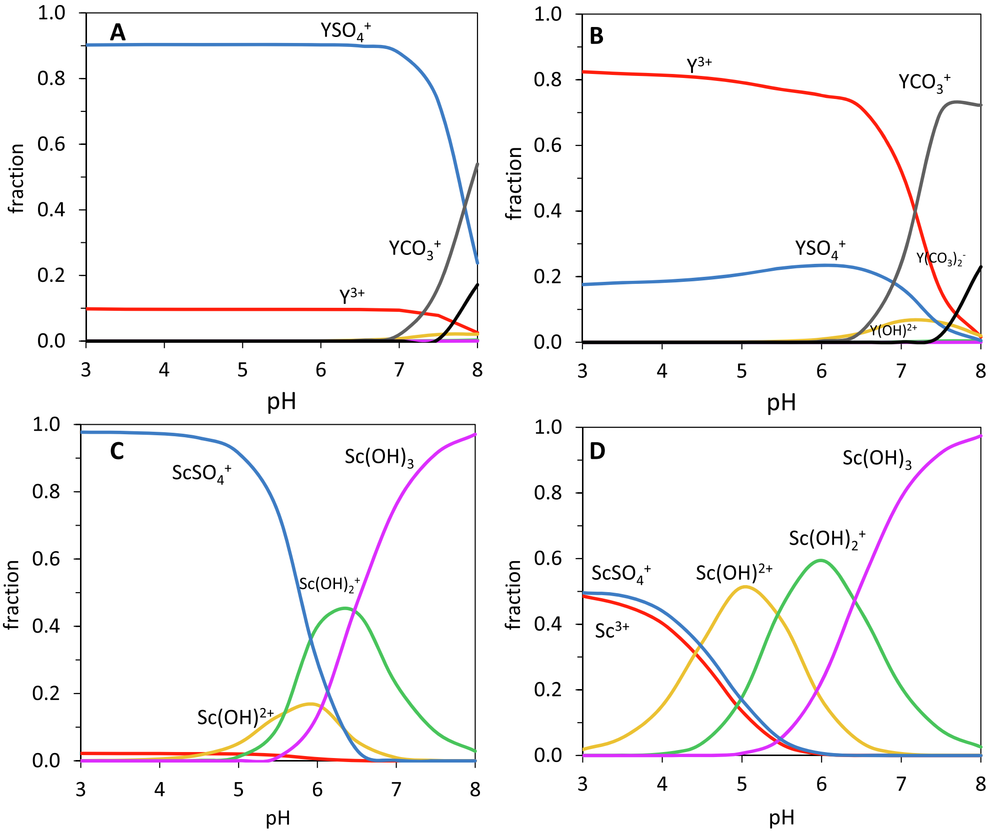

Fig. 4. Aqueous species distribution of Y and Sc with pH for a solution with 20 mM (A, C) and 0.5 mM (B, D) of sulfate at 25 °C and atmospheric pCO_2.

where a_{Mz+} and a_{H+} are the activities of the aqueous complex and proton, respectively; and $\{(XO)_nM^{z-n}\}$ and $\{XOH\}$ account for the mole fraction of the sorbed species ($[(XO)_nM^{z-n}]/[T_{XOH}]$) and the free surface sites ($[XOH]/T_{XOH}$), respectively.

A total surface site concentration T_{XOH} of 516 μmol/kg was obtained from the basaluminite site density of 4.6 site/nm^{-2}, the specific surface area of 68 m^2/g. The concentration of free surface sites was calculated as:

$$[XOH] \;=\; T_{XOH} - \sum n[(XO)_nM^{z-n}] \tag{5}$$

The value of the equilibrium constant K_M for each element was obtained with data from the experiment with 20 mM SO_4, except for the case of the species $Sc(OH)^{2+}$, which was obtained from the experiment with 0.5 mM SO_4.

Thus, replacing the molar fraction by their values, taking logarithms of Eq. (4) and rearranging the order we obtain a linear expression (Eq. (6)):

$$\log\frac{[(XO)_nM^{z-n}]}{a_{M^{z+}}} = \log K_M + npH + n\log[XOH] - (n-1)\log T_{XOH} \tag{6}$$

The term for total surface sites (T_{XOH}) is only discarded for monodentate surface complexes (n=1) but it must be accounted for multidentate surface complexes. For instance, when bidentante complexes (n = 2) are present, the Eq. (6) is rearranged as expressed in Eq. (7).

The equilibrium constants for bidentate surface complexes are those referred to as the K_3 according to the model 3 proposed by Wang and Giammar (2013), where $K_3 = K_1 \cdot T_{XOH}$.

$$\log\frac{[(XO)_nM^{z-n}]}{a_{M^{z+}}} = \log K_M + 2pH + 2\log[XOH] + \log T_{XOH} \tag{7}$$

By plotting the experimental data according to Eqs. (6) and (7), linear correlations were obtained. Except for Sc, the slope of the regression was close to 1, where only La showed a slope value below 1. For the rest of lanthanides, the slopes were higher than 1 and increased progressively from LREE to HREE, reaching up to 1.3 (Fig. 5). A slope close to 1 suggests that the sorption occurs as a monodentate complex as indicated by the Eq. (3) with n = 1 (Rabung et al., 1998 and 2000). Similar observations were obtained by Rabung et al. (2006), after fitting EXAFS spectra of a γ-Al_2O_3 sorbed with Lu, where Lu formed a monodentate inner sphere complex.

Unlike Y and the lanthanides, the linear regression for $ScSO_4^+$ data from the 20 mM SO_4 experiment resulted in a slope close to 2 (2.37) (Fig. 6A). Similar results were observed for $Sc(OH)^{2+}$ with a slope of 1.90 from the experiment with 0.5 mM SO_4, where it was the major species (Fig. 6B). In both cases, a slope of 2 suggests exchange with two surface protons and formation of a bidentate surface complex for both aqueous species. Despite the fact that

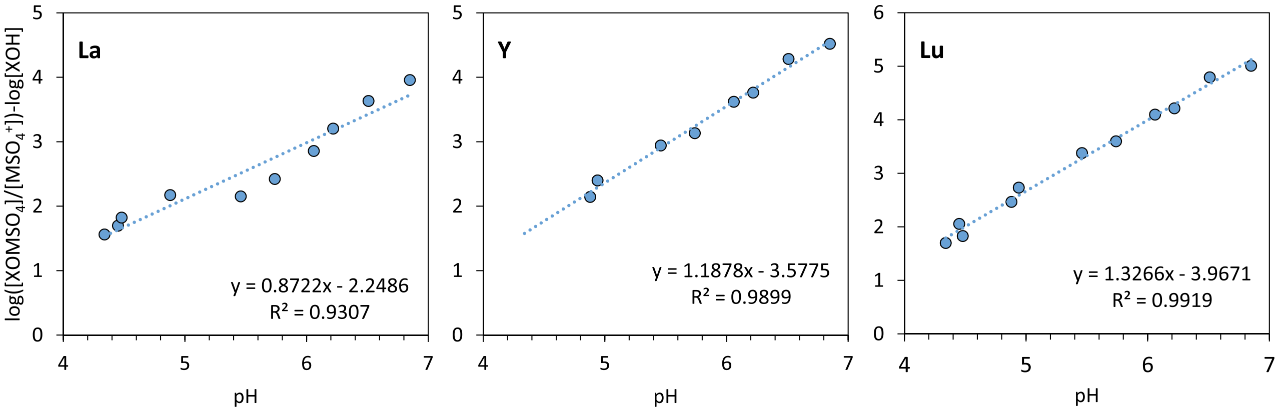

Fig. 5. Regressions obtained from the experimental data plotted as Eq. (6) considering n = 1. Measured pH values and activities calculated from the final concentrations. XOH are free available surface sites.

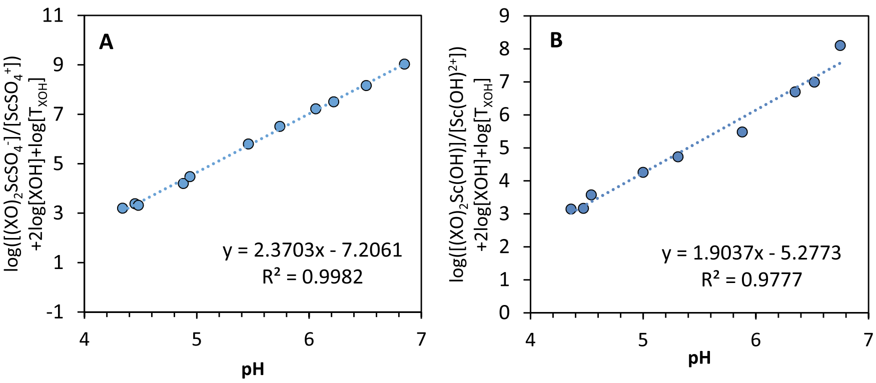

Fig. 6. Regressions obtained from experimental data from Sc element plotted according the linearized equations of reaction (7) (n = 2) for $ScSO_4^+$ (A) and for $Sc(OH)_2^+$ (B).

$Sc(OH)_2^+$ was predominant at pH 5.5, this aqueous species provided a very low slope and poorer correlation (not shown), and was not considered a sorbed species.

To obtain surface sorption constants, the regression slopes were forced to 1 for yttrium and lanthanides and to 2 for Sc via the Gnuplot v5.00 software (Williams and Kelley, 1986) using experimental data with higher sulfate content in solution. The resulting log K_M was obtained as the intercept. The error of the regression calculation was larger and enclosed the analytical error, and it was assumed to be the error of the log K_M value. The log K_M values and the regression errors for surface complexation reactions for all REE are listed in Table 1. Apart from values for Sc complexation, the equilibrium constants increased from −2.48 to −2.19 from La to Lu, indicating higher HREE than LREE affinity for the basaluminite surface. These log K_M values are close to those obtained by Quinn et al. (2006a) for complexation of free REE ions onto ferric oxide surfaces.

4.3. Validation

Log K_M values conducted at high sulfate concentration were validated with results from the experiment with lower

Table 1

Equilibrium constants for the formation of surface complexes (K_M of Eq. (3)) obtained by fitting the experimental values. Concentration of the surface species calculated as their molar fractions (i.e., K_M is the K_3 value of Wang and Giammar (2013)). Surface site density was 4.60 nm^{-2} and specific surface area 68 m^2/g.

Element	Surface Complex	Log K_M	Error
Sc	$(XO)_2ScSO_4^-$	−5.19	0.08
	$(XO)_2Sc(OH)$	−5.81	0.09
Y	$XOYSO_4$	−2.48	0.06
La	$XOLaSO_4$	−2.95	0.08
Ce	$XOCeSO_4$	−2.81	0.07
Pr	$XOPrSO_4$	−2.69	0.05
Nd	$XONdSO_4$	−2.60	0.03
Sm	$XOSmSO_4$	−2.48	0.05
Eu	$XOEuSO_4$	−2.50	0.05
Gd	$XOGdSO_4$	−2.50	0.04
Tb	$XOTbSO_4$	−2.48	0.06
Dy	$XODySO_4$	−2.37	0.06
Ho	$XOHoSO_4$	−2.40	0.05
Er	$XOErSO_4$	−2.40	0.11
Tm	$XOTmSO_4$	−2.27	0.08
Yb	$XOYbSO_4$	−2.13	0.08
Lu	$XOLuSO_4$	−2.19	0.09

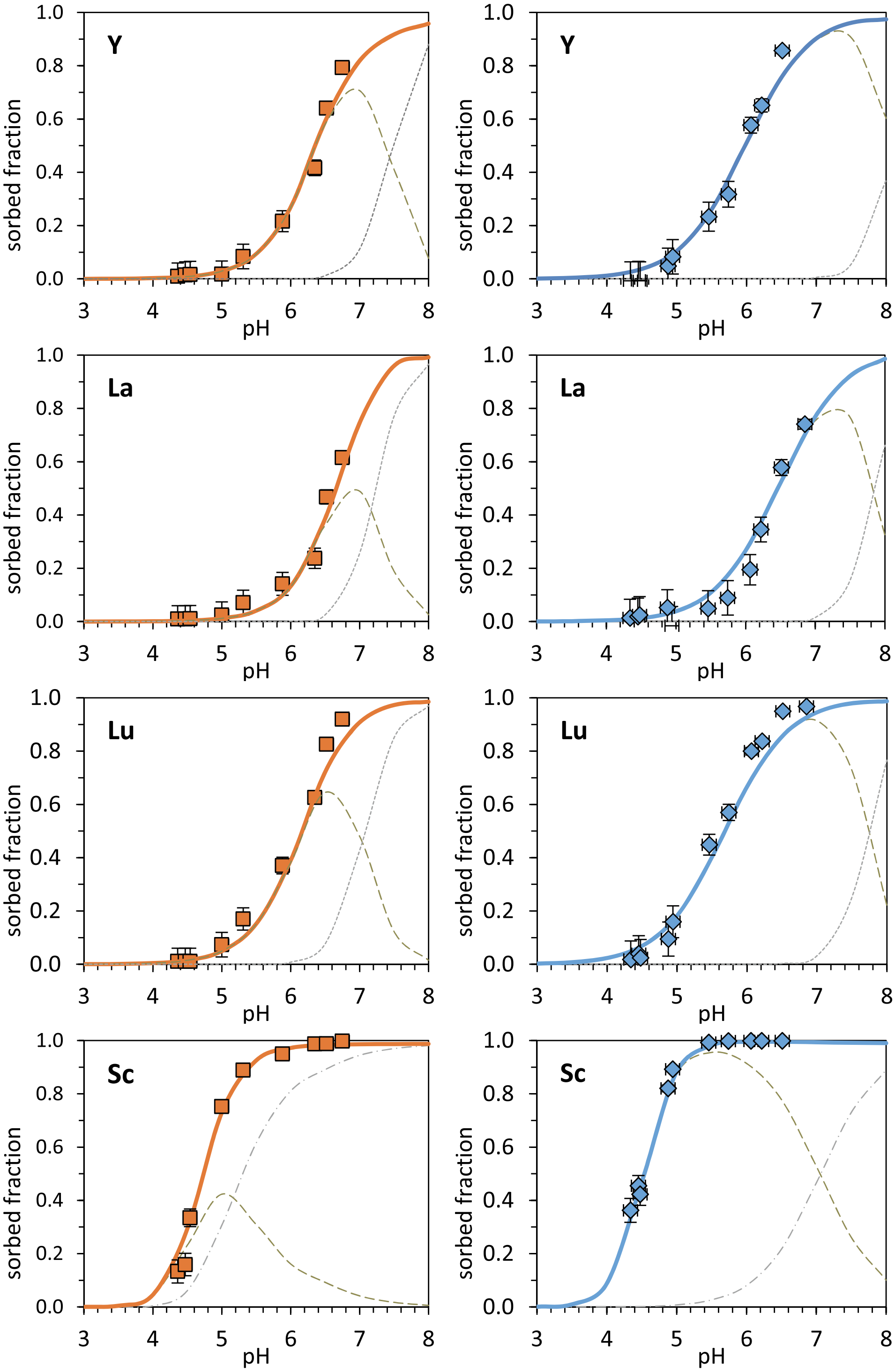

Fig. 7. Comparison between experimental data (symbols) and calculated fraction (lines) of the sorption edge curves for Sc, Y, La and Lu of the experiments with 20 mM SO_4 (diamonds) and with 0.5 mM SO_4 (squares). Continuous lines: total sorption, dashed lines: sorption of MSO_4^+ species and pointed lines: sorption of MCO_3^+. Calculations at 25 °C and pCO_2 of 3.5, including the carbonate complexation constants listed in Table SI-6.

sulfate content. In the case of Sc, the log K_M of reaction (7), obtained from the experiments with low sulfate content, was used to predict of the sorption edge curves for the 20 mM SO_4 experiment. The model results are plotted with continuous lines in Fig. 7. Model results for each REE are plotted in Figs. SI-3 and SI-4.

A temperature of 25 °C and a pCO_2 of 3.5 was considered to reproduce room conditions in the sorption models. At higher pH values than 6.5 a mismatch between the modeled sorbed fractions (solid lines in Fig. 7) and the experimental ones (symbols) for the experiment with the lower sulfate content is attributed to the presence of dissolved carbonate species. Thus, MCO_3^+ species can take part in the sorption process. To show the possible role of carbonate complexes at pH higher than 6.5 and low sulfate concentration, the sorption of MCO_3^+ complexes has been included in the model. The equilibrium constants for the MCO_3^+ sorption reactions have been recalculated from those reported by Quinn et al. (2006b) for goethite (Table SI-6). Including carbonate complexation, the model predicts sorption at near neutral pH when lower sulfate is present in solution, supporting the role of carbonate complexation at such particular conditions (pointed lines in Fig. 7).

As expected, the model reproduces the sorption edges in the experiment with 20 mM SO_4 (Fig. 7, left) well. Indeed, only adsorption very close or outside the experimental error is predicted for La and Ce at some pH values below 6.0. Although worse, the model for the experiment with lower sulfate content is also acceptable, and the predicted values in general fit the analyses within experimental error (Fig. 7, right). A slight overprediction of the adsorption at intermediate pH values and an underprediction at high pH values is systematically observed.

In addition to the sorption edges, the model also predicts the fractionation patterns of the lanthanide group (Fig. SI-5) and the M-type tetrad effect, within experimental error. As observed in the pH sorption edge curves, the model tends to underpredict the K_D values at pH 6.4. This is especially relevant for low sulfate concentration (Fig. SI-5B) and is attributed to the increasing importance of MCO_3^+ aqueous complexes at near neutral pH. In contrast, the model tends to overpredict the values for the intermediate pH (between 5.5 and 6.5), particularly for the intermediate lanthanides. The yttrium experimental K_D values are well predicted in all cases. However, the model fails to predict other anomalies. For instance, the positive Ce anomaly observed at pH values lower than 5.3 in the experiment without an initial sulfate concentration is not reproduced. Similar observations were described in Bau (1999) for REE scavenged in Fe oxyhydroxide at a pH lower than 5 and were attributed to a partial oxidation of Ce(III) at low pH. Similar poor fit is observed for the Er negative anomaly in sorption with high sulfate in solution and, the Dy and Yb negative anomalies detected with lower aqueous sulfate concentrations were not predicted by the model. In the latter case, no previous descriptions of these anomalies have been reported and they might be related to an analytical error for very low concentration.

The good fit between the predicted and measured Sc values confirms a good model prediction for the formation of

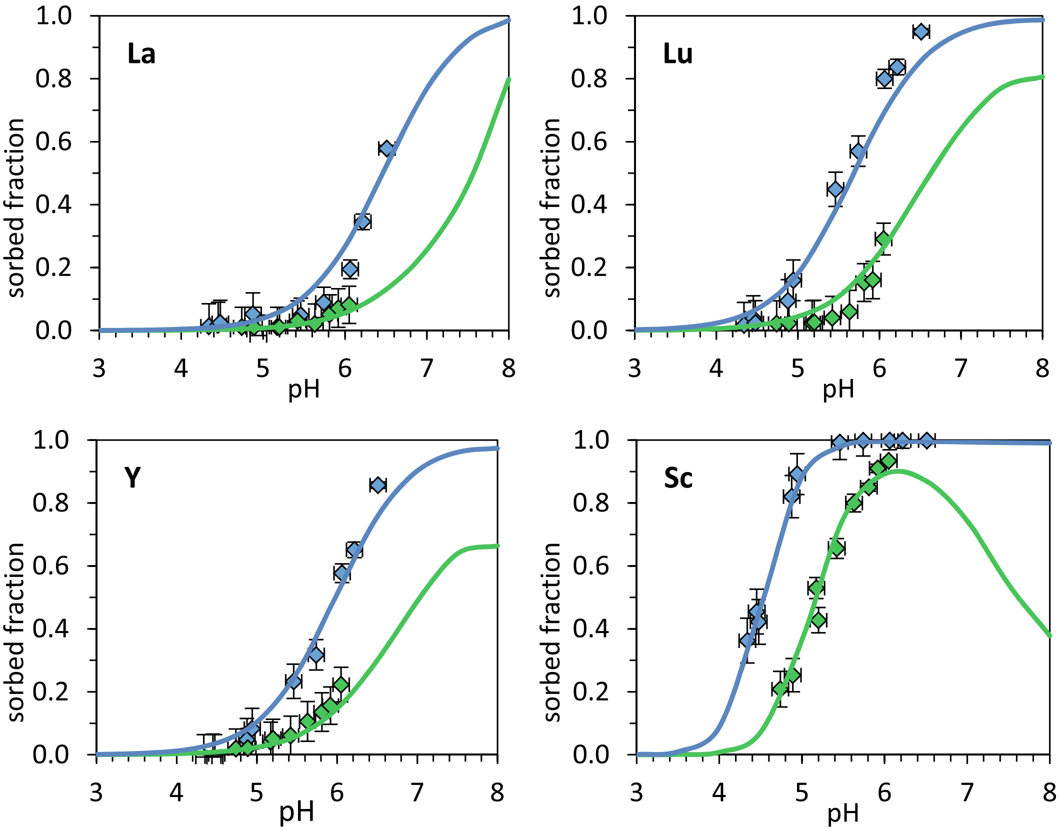

Fig. 8. Comparison between experimental data (symbols) and calculated fraction (lines of the sorption edge curves for Sc, Y, La and Lu at two different solid:liquid ratios (1 g/L the blue symbols and 0.25 g/L the green ones) and 20 mM SO_4. Calculations at 25 °C and pCO_2 of 3.5, including the carbonate complexation constants listed in Table SI-6.

bidentate surface complexes. As observed in Fig. 7, the $(XO)_2ScSO_4^-$ complex predominates in the experiment with 20 mM SO_4, and the $(XO)_2ScOH$ complex predominates in the experiment with a low SO_4 concentration. Again, Sc behaves differently due to the stronger hydrolysis effect than sulfate complexation. The higher ligand ratio for Sc may be due to its structural characteristics. Lanthanide cations are larger than Sc^{3+}, and have coordination numbers ranging from 8 (with a tricaped trigonal prism configuration) to 9 (with a distorted square antiprism or dodecahedron configuration of the hydration sphere) (Lindqvist-Reis et al., 2000; Rouse et al., 2001). On the contrary, Sc^{3+} (0.75 Å) has an ionic radius closer to that of Al^{3+} (0.53 Å), adopting an octahedral coordination (Lindqvist-Reis et al., 2006; Levard et al., 2018). This fact leads to similar interatomic distances to oxygen, allowing the formation of complexes with bidentate ligands. The different behavior of Sc suggests its potential segregation from the rest of the REE.

Finally, the model was also tested with experimental data for a solid:liquid ratio of 0.25 g/L. The results for four selected elements are included in Fig. 8 (the results for the initial ratio of 1 g/L are also included). The comparison between predicted and experimental values for the complete set of REE is in Fig. SI-6. As expected, the model predicts lower adsorption for lower solid:liquid ratio, showing a general consistency with experimental data. Comparing the prediction along the lanthanide series with experimental sorption data, the model better predicts HREE than LREE, where the predicted sorption was slightly lower than observed for La, Ce and Pr. Interestingly, Sc sorption by means of bidentate complexes was satisfactory predicted.

5. CONCLUSIONS

This work shows that basaluminite has a high capacity to retain REE by an adsorption mechanism, and this process is highly dependent on pH. Thus, REE sorption on basaluminite starts to be significant between pH 5–5.5 for lanthanides and yttrium and from pH 4–4.5 for Sc, depending on the solid:liquid ratio. Lanthanide fractionation also occurred from pH 5.3, yielding the M-type tetrad effect and reflecting HREE enrichment onto the solid. These results are analogous to the fractionation observed in Al and Fe oxide precipitates in the confluence of acid sulfate waters with natural streams and rivers and therefore could explain the mechanism of REE retention in natural precipitates. As expected from the overwhelming importance of the sulfate aqueous speciation (MSO_4^+), higher REE sorption was observed at higher sulfate concentrations. These results confirm that aqueous speciation and sorption onto basaluminite control the REE geochemistry in acid rock/mine drainages.

A non-electrostatic surface complexation model has been proposed to explain the sorption mechanism. In the model description, sulfate plays a key role since the strong complexation with REE leads to sorption of the aqueous sulfate complex MSO_4^+, rather than the free ion M^{3+}, as commonly described by other authors for REE sorption in oxides. Thanks to experimental data from the REE sorption experiment with high sulfate concentration (20 mM), surface constants were calculated and validated with experiments with low sulfate concentration (0.1 to 0.9 mM) and a lower solid:liquid ratio. Additionally, at near neutral pH and sulfate concentrations lower than 1 mM, the sorption of the aqueous carbonate complex, MCO_3^+, should be considered when mixing with natural water.

This work presents for the first time sorption equilibrium constants for REE sorption onto basaluminite, a very common mineral in mine discharge. Despite REE behaving as a group with similar chemical properties, their ionic radii vary along the series, and the different distances lead to slightly different positions on the basaluminite surface. This is clearly observed for Sc, which with a considerably smaller ionic radius than the other REE, forms bidentate surface complexes in comparison with the monodenate bonds formed by the rest of the REE group. Additionally, its aqueous speciation, with the formation of stable hydroxyl species, makes Sc behave differently and sorb at lower pH values. This knowledge could help design REE separation mechanisms and isolate cost-effective elements.

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gca.2019.05.016.

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Supplementary material

Sorption of rare earth elements onto basaluminite: the role of sulfate and pH

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TABLE CAPTIONS

Table SI-1. Aqueous speciation constants for Sc, Y and lanthanides (M) with different ligands. References: [a]: Klugness & Byrne, 2000 ; [b]: Lee & Byrne, 92; [c]: Luo & Byrne, 2004;[d]: Millero, 1992; [e]: Luo & Millero, 2004; [f]: Schijf & Byrne, 2004; [g]: Luo & Byrne,2001; [h]: Wood and Samson, 2006 (for Sc speciation).

Table SI-2. Initial and final concentrations (mg/L) of aqueous solution at each pH for the two sets of experiments with solid:liquid ratio of 1 g/L and 0.5 mM SO_4 and 20 mM SO_4, respectively.

Table SI-3. Saturation index (SI) for experiment with 20 mM SO_4 and 0.5 mM SO_4, respectively.

Table SI-4. Sorbed fraction calculated with data from the experiments with a 0.25 g/L solid:liquid ratio and 20 mM SO_4 in solution.

Table SI-5. Experimental log K_D (L/kg) from experiment with 20 mM SO_4 and 0.5 mM SO_4, respectively.

Table SI-6. REE surface complexation constants for aqueous carbonate complexes estimated from values obtained by Quinn et al., 2006 b (Table2).

FIGURE CAPTIONS

Fig. SI-1. X-ray Diffraction Pattern for synthetic basaluminite previous to sorption experiments (pure) and basaluminite after REE adsorption with sulfate presence at four different pH values obtained at ID-31 beamline, ESRF. The peaks observed are artifacts due to the panel detector (see Lozano et al., 2018 for details).

Fig. SI-2. Distribution of the surface sites in basaluminite structure.

Fig. SI-3. Predictions of REE adsorption in experiment with 20 mM sulfate using surface complexation constants in table 2.

Fig. SI-4. Predictions of REE adsorption in experiment with 0.5 mM sulfate using surface complexation constants in table 2.

Fig. SI-5. Experimental data (symbols) and model (lines) of fractionation constants (log K_D) for lanthanide series in (A) sorption experiment without 20 mM sulfate and (B) with 0.5 mM sulfate. Calculations at 25 C and pCO_2 of 3.5 including sorption of both MSO_4^+ and MCO_3^+ aqueous species.

Fig SI-6. REE sorption fraction for two different solid:solute ratios 1 g/L (blue), 0.25 g/L (green) obtained from experimental data (symbols) and the predicted model for each experiment (lines).

Table SI-1. Aqueous speciation constants for Sc, Y and lanthanides (M) with different ligands. References: [a]: Klugness & Byrne, 2000 ; [b]: Lee & Byrne, 92; [c]: Luo & Byrne, 2004;[d]: Millero, 1992; [e]: Luo & Millero, 2004; [f]: Schijf & Byrne, 2004; [g]: Luo & Byrne,2001; [h]: Wood and Samson, 2006 (for Sc speciation).

Equation	**$\log {}_{L}\beta_{n}$**	**Sc**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Ref**
$M^{+3} + H_2O = M(OH)^{+2} + H^+$	$\log {}_{OH}\beta^*{}_1$	-4.31	-7.80	-8.81	-8.34	-8.32	-8.18	-7.84	-7.76	-7.83	-7.64	-7.59	-7.56	-7.52	-7.39	-7.45	-7.27	a
$M^{+3} + 2H_2O = M(OH)_2{}^+ + 2H^+$	$\log {}_{OH}\beta^*{}_2$	-9.70	-16.40	-18.14	-17.60	-17.27	-17.04	-16.51	-16.37	-16.37	-16.18	-16.10	-16.07	-15.96	-15.88	-15.74	-15.67	b,h
$M^{+3} + 3H_2O = M(OH)_3 + 3H^+$	$\log {}_{OH}\beta^*{}_3$	-16.10	-25.99	-27.90	-27.23	-26.63	-26.40	-25.91	-25.41	-25.28	-25.08	-24.83	-24.56	-24.35	-24.18	-23.85	-23.85	b,h
$M^{+3} + CO_3{}^{-2} = MCO_3{}^+$	$\log {}_{CO3}\beta_1$		7.48	6.73	7.06	7.23	7.28	7.46	7.48	7.39	7.46	7.56	7.55	7.61	7.68	7.81	7.75	c
$M^{+3} + HCO_3{}^- = MHCO_3{}^{+3}$	$\log {}_{HCO3}\beta_1$		2.32	2.34	2.31	2.25	2.28	2.34	2.47	2.36	2.46	2.50	2.46	2.49	2.52	2.53	2.49	c
$M^{+3} + 2CO_3{}^{-2} = M(CO3)_2{}^-$	$\log {}_{CO3}\beta_2$		12.63	11.30	11.76	12.08	12.17	12.53	12.63	12.48	12.78	12.91	13.00	13.12	13.27	13.30	13.37	c
$M^{+3} + NO_3{}^- = MNO_3{}^{+2}$	$\log {}_{NO3}\beta_1$			0.58	0.69	0.69	0.79	0.78	0.83	0.47	0.51	0.15	0.25	0.15	0.20	0.25	0.56	d
$M^{+3} + F^- = MF^{+2}$	$\log {}_{F}\beta_1$		3.97	3.11	3.29	3.35	3.29	3.61	3.72	3.71	3.83	3.88	3.78	3.77	3.77	3.84	3.74	e
$M^{+3} + 2F^- = MF_2{}^+$	$\log {}_{F}\beta_2$		6.35	5.16	5.48	5.66	5.66	5.99	6.11	6.07	6.24	6.29	5.98	5.96	6.09	6.31	6.31	e
$M^{+3} + SO_4{}^{-2} = MSO_4{}^+$	$\log {}_{so4}\beta_1$	4.18	3.50	3.61	3.61	3.62	3.60	3.63	3.64	3.61	3.59	3.57	3.54	3.51	3.48	3.46	3.44	f,h
$M^{+3} + Cl^- = MCl^{+2}$	$\log {}_{Cl}\beta_1$		0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	g

Table SI-2. Initial and final concentrations (ppm) of aqueous solution at each pH for experiment with solid:liquid ratio of 1 g/L and 0.5 mM SO_4 and 20 mM SO_4, respectively.

Sorption with 20 mM SO_4 in solution

Initial concentration (ppm)

pH	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Al	S	Na
4.34	0.957	0.960	0.872	0.874	0.890	0.948	0.954	0.937	0.942	0.945	0.997	0.951	0.901	0.947	0.963	0.950	0.00	665.80	957.09
4.45	0.943	0.946	0.859	0.861	0.877	0.934	0.940	0.923	0.928	0.931	0.983	0.937	0.887	0.933	0.949	0.936	0.00	665.80	957.09
4.48	0.928	0.930	0.846	0.847	0.863	0.919	0.925	0.908	0.913	0.916	0.967	0.922	0.873	0.919	0.934	0.921	0.00	665.80	957.09
4.88	0.919	0.921	0.838	0.839	0.855	0.911	0.916	0.900	0.905	0.908	0.958	0.914	0.865	0.910	0.925	0.912	0.00	665.80	957.09
4.94	0.916	0.918	0.834	0.836	0.852	0.907	0.913	0.897	0.901	0.904	0.954	0.910	0.862	0.907	0.922	0.909	0.00	665.80	957.09
5.46	0.905	0.908	0.845	0.826	0.842	0.896	0.902	0.886	0.891	0.894	0.943	0.899	0.852	0.896	0.911	0.898	0.00	665.80	957.09
5.74	0.900	0.902	0.820	0.822	0.837	0.891	0.897	0.881	0.885	0.888	0.938	0.894	0.847	0.891	0.906	0.893	0.00	665.80	957.09
6.06	0.891	0.894	0.812	0.813	0.829	0.882	0.888	0.872	0.877	0.880	0.929	0.885	0.839	0.882	0.897	0.884	0.00	665.80	957.09
6.22	0.891	0.895	0.813	0.814	0.829	0.883	0.889	0.873	0.877	0.880	0.929	0.886	0.839	0.883	0.898	0.885	0.00	665.80	957.09
6.51	0.876	0.879	0.799	0.800	0.815	0.868	0.874	0.858	0.863	0.865	0.914	0.871	0.825	0.868	0.882	0.870	0.00	665.80	957.09
6.85	0.876	0.879	0.799	0.800	0.815	0.868	0.874	0.858	0.863	0.865	0.914	0.871	0.825	0.868	0.882	0.870	0.00	665.80	957.09

Final concentration (ppm)

pH	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Al	S	Na
4.34	0.61	0.967	0.86	0.868	0.883	0.936	0.941	0.921	0.927	0.934	0.98	0.934	0.885	0.931	0.939	0.933	14.780	580.13	832.37
4.45	0.514	0.951	0.843	0.84	0.86	0.911	0.913	0.898	0.903	0.905	0.95	0.907	0.891	0.898	0.903	0.899	8.485	585.95	840.73
4.48	0.536	0.937	0.825	0.827	0.847	0.895	0.899	0.883	0.886	0.897	0.938	0.897	0.947	0.896	0.905	0.899	9.720	584.65	838.86
4.88	0.165	0.877	0.794	0.792	0.803	0.853	0.853	0.841	0.838	0.848	0.881	0.849	0.886	0.83	0.824	0.826	0.685	583.98	837.89
4.94	0.099	0.842	0.847	0.76	0.775	0.82	0.811	0.803	0.809	0.809	0.84	0.806	0.835	0.782	0.764	0.764	0.220	579.83	831.94
5.46	0.007	0.696	0.804	0.767	0.685	0.716	0.665	0.704	0.678	0.642	0.642	0.625	0.62	0.548	0.481	0.495	0.000	565.05	810.74
5.74	0.002	0.616	0.747	0.723	0.633	0.655	0.588	0.616	0.611	0.558	0.543	0.537	0.513	0.44	0.371	0.384	0.000	553.60	794.31
6.06	0.001	0.378	0.654	0.539	0.466	0.457	0.358	0.363	0.388	0.343	0.298	0.312	0.267	0.223	0.164	0.177	0.000	538.90	773.22
6.22	0.001	0.312	0.532	0.432	0.393	0.369	0.289	0.293	0.316	0.276	0.242	0.253	0.219	0.182	0.136	0.144	0.000	551.25	790.94
6.51	0.001	0.126	0.337	0.227	0.185	0.17	0.115	0.112	0.132	0.101	0.088	0.09	0.076	0.059	0.043	0.044	0.000	562.85	807.58
6.85	0.001	0.079	0.207	0.137	0.112	0.105	0.072	0.07	0.082	0.064	0.056	0.057	0.048	0.038	0.028	0.028	0.000	570.38	818.38

Table SI-2. continuation

Sorption with 0.5 mMSO$_4$ in solution																			
Initial concentration (ppm)																			
pH	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Al	S	Na
4.36	0.898	0.898	0.891	0.896	0.886	0.886	0.889	0.880	0.884	0.882	0.883	0.879	0.881	0.883	0.886	0.881	0.000	0.000	0.000
4.47	0.878	0.878	0.871	0.875	0.866	0.865	0.869	0.860	0.864	0.862	0.863	0.859	0.861	0.863	0.865	0.861	0.000	0.000	0.000
4.54	0.890	0.890	0.883	0.887	0.878	0.877	0.881	0.872	0.875	0.874	0.875	0.871	0.872	0.875	0.877	0.872	0.000	0.000	0.000
5.00	0.881	0.881	0.874	0.878	0.869	0.868	0.872	0.863	0.867	0.865	0.866	0.862	0.864	0.866	0.868	0.864	0.000	0.000	0.000
5.31	0.873	0.873	0.867	0.871	0.861	0.861	0.864	0.855	0.859	0.857	0.859	0.854	0.855	0.859	0.861	0.855	0.000	0.000	0.000
5.88	0.949	0.949	0.941	0.946	0.936	0.936	0.939	0.930	0.934	0.932	0.933	0.929	0.930	0.933	0.936	0.930	0.000	0.000	0.000
6.35	0.943	0.943	0.936	0.941	0.930	0.930	0.934	0.925	0.928	0.926	0.928	0.923	0.925	0.928	0.930	0.925	0.000	0.000	0.000
6.52	0.911	0.878	0.891	0.881	0.837	0.840	0.834	0.832	0.820	0.836	0.868	0.831	0.875	0.838	0.866	0.838	0.000	0.000	0.000
6.75	0.870	0.870	0.864	0.868	0.859	0.857	0.862	0.852	0.856	0.854	0.855	0.851	0.853	0.855	0.857	0.853	0.000	0.000	0.000
8.40	0.862	0.830	0.842	0.833	0.792	0.795	0.789	0.787	0.776	0.791	0.820	0.786	0.827	0.792	0.818	0.792	0.000	0.000	0.000
Final concentration (ppm)																			
pH	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Al	S	Na
4.36	0.778	0.889	0.882	0.877	0.877	0.870	0.871	0.869	0.856	0.868	0.874	0.862	0.863	0.866	0.877	0.871	4.765	8.219	0.731
4.47	0.738	0.865	0.862	0.856	0.856	0.853	0.850	0.849	0.855	0.845	0.854	0.850	0.852	0.854	0.856	0.851	3.993	9.328	0.752
4.54	0.592	0.875	0.873	0.865	0.865	0.868	0.872	0.860	0.853	0.855	0.866	0.862	0.863	0.866	0.868	0.862	2.629	9.808	0.760
5.00	0.218	0.865	0.852	0.845	0.844	0.833	0.827	0.824	0.818	0.822	0.855	0.819	0.815	0.811	0.859	0.800	0.513	10.752	0.857
5.31	0.097	0.801	0.805	0.791	0.789	0.770	0.760	0.751	0.731	0.751	0.800	0.747	0.738	0.726	0.760	0.710	0.045	12.619	0.817
5.88	0.048	0.746	0.808	0.788	0.778	0.764	0.735	0.724	0.719	0.724	0.770	0.719	0.754	0.690	0.710	0.585	0.000	17.285	0.603
6.35	0.012	0.550	0.714	0.630	0.542	0.493	0.444	0.460	0.472	0.439	0.446	0.431	0.433	0.382	0.362	0.346	0.000	22.295	1.098
6.52	0.011	0.315	0.474	0.355	0.316	0.284	0.210	0.210	0.243	0.217	0.210	0.213	0.205	0.174	0.148	0.146	0.000	30.200	0.000
6.75	0.002	0.180	0.332	0.226	0.179	0.150	0.099	0.099	0.124	0.103	0.103	0.105	0.102	0.083	0.071	0.068	0.000	28.945	1.259
8.40	0.004	0.002	0.002	0.002	0.001	0.002	0.001	0.001	0.001	0.001	0.002	0.001	0.002	0.001	0.002	0.001	0.000	44.952	0.000

Table SI-3. Saturation index (SI) for experiment with 20 mM SO_4 and 0.5 mM SO_4, respectively.

	experiment with 20 mM SO_4									
pH	4.34	4.45	4.48	4.88	4.94	5.46	5.74	6.06	6.22	6.51	6.85
Basaluminite	0.7	0.8	1.3	0.6	-0.8	-	-	-	-	-	-
Gibbsite$_{(am)}$	-2.0	-1.9	-1.8	-1.8	-2.1	-	-	-	-	-	-
Alunite(Na)	4.5	4.5	4.8	3.6	2.5	-	-	-	-	-	-
Y(OH)$_{3(am)}$	-12.4	-12.1	-12.0	-10.9	-10.7	-9.2	-8.4	-7.6	-7.3	-6.8	-6.0
La(OH)$_{3(am)}$	-17.2	-16.9	-16.9	-15.7	-15.5	-13.9	-13.1	-12.2	-11.8	-11.1	-10.3
Ce(OH)$_{3(am)}$	-15.0	-14.7	-14.7	-13.5	-13.3	-11.7	-10.9	-10.1	-9.7	-9.1	-8.3
Pr(OH)$_{3(am)}$	-14.8	-14.5	-14.5	-13.3	-13.1	-11.6	-10.8	-9.9	-9.6	-9.0	-8.2
Nd(OH)$_{3(am)}$	-14.2	-13.9	-13.8	-12.7	-12.5	-11.0	-10.2	-9.3	-9.0	-8.4	-7.6
Sm(OH)$_{3(am)}$	-12.4	-12.0	-12.0	-10.8	-10.6	-9.2	-8.3	-7.6	-7.2	-6.8	-6.0
Gd(OH)$_{3(am)}$	-11.8	-11.5	-11.4	-10.2	-10.0	-8.6	-7.8	-7.0	-6.6	-6.1	-5.3
Tb(OH)$_{3(am)}$	-12.5	-12.2	-12.2	-11.0	-10.8	-9.4	-8.6	-7.8	-7.4	-7.0	-6.2
Dy(OH)$_{3(am)}$	-11.2	-10.9	-10.8	-9.7	-9.5	-8.1	-7.3	-6.6	-6.2	-5.8	-5.0
Ho(OH)$_{3(am)}$	-11.5	-11.2	-11.1	-10.0	-9.8	-8.3	-7.5	-6.8	-6.5	-6.0	-5.2
Er(OH)$_{3(am)}$	-12.7	-12.4	-12.3	-11.1	-11.0	-9.5	-8.7	-8.1	-7.7	-7.3	-6.5
Tm(OH)$_{3(am)}$	-11.0	-10.7	-10.6	-9.4	-9.3	-7.9	-7.1	-6.4	-6.1	-5.7	-4.9
Yb(OH)$_{3(am)}$	-12.7	-12.3	-12.3	-11.1	-11.0	-9.6	-8.9	-8.3	-7.9	-7.5	-6.7
Lu(OH)$_{3(am)}$	-12.7	-12.3	-12.3	-11.1	-10.9	-9.6	-8.8	-8.2	-7.8	-7.5	-6.7
Y(OH)$_3$	-10.9	-10.6	-10.5	-9.4	-9.2	-7.7	-6.9	-6.1	-5.8	-5.3	-4.5
La(OH)$_3$	-14.0	-13.7	-13.7	-12.5	-12.3	-10.7	-9.9	-9.0	-8.6	-7.9	-7.1
Ce(OH)$_3$	-13.7	-13.4	-13.4	-12.2	-12.0	-10.4	-9.6	-8.8	-8.4	-7.8	-7.0
Pr(OH)$_3$	-13.3	-13.0	-13.0	-11.8	-11.6	-10.1	-9.3	-8.4	-8.1	-7.5	-6.7
Nd(OH)$_3$	-11.8	-11.5	-11.4	-10.3	-10.1	-8.6	-7.8	-6.9	-6.6	-6.0	-5.2
Sm(OH)$_3$	-10.3	-9.9	-9.9	-8.7	-8.5	-7.1	-6.2	-5.5	-5.1	-4.7	-3.9
Eu(OH)$_3$	-9.1	-8.8	-8.8	-7.6	-7.4	-5.9	-5.1	-4.4	-4.0	-3.6	-2.7
Gd(OH)$_3$	-9.4	-9.1	-9.0	-7.8	-7.6	-6.2	-5.4	-4.6	-4.2	-3.7	-2.9
Tb(OH)$_3$	-9.4	-9.1	-9.1	-7.9	-7.7	-6.3	-5.5	-4.7	-4.3	-3.9	-3.1
Dy(OH)$_3$	-9.6	-9.3	-9.2	-8.1	-7.9	-6.5	-5.7	-5.0	-4.6	-4.2	-3.4
Ho(OH)$_3$	-9.1	-8.8	-8.7	-7.6	-7.4	-5.9	-5.1	-4.4	-4.1	-3.6	-2.8
Er(OH)$_3$	-8.7	-8.4	-8.3	-7.1	-7.0	-5.5	-4.7	-4.1	-3.7	-3.3	-2.5
Tm(OH)$_3$	-8.7	-8.4	-8.3	-7.1	-7.0	-5.6	-4.8	-4.1	-3.8	-3.4	-2.6
Yb(OH)$_3$	-8.4	-8.0	-8.0	-6.8	-6.7	-5.3	-4.6	-4.0	-3.6	-3.2	-2.4
Lu(OH)$_3$	-8.2	-7.8	-7.8	-6.6	-6.4	-5.1	-4.3	-3.7	-3.3	-3.0	-2.2
Sc(OH)$_3$	-6.3	-6.0	-5.9	-5.2	-5.3	-5.0	-4.8	-4.6	-4.4	-4.1	-4.0

Table SI-3. continuation

	experiment with 0.5 mM SO_4									
pH	4.36	4.47	4.54	5.00	5.31	5.88	6.35	6.52	6.75	8.40
Basaluminite	1.1	1.9	1.8	3.0	-	-	-	-	-	-
$Gibbsite_{(am)}$	-1.5	-1.3	-1.3	-0.8	-	-	-	-	-	-
Alunite(Na)	-0.1	0.4	0.3	0.6	-	-	-	-	-	-
$Y(OH)_{3(am)}$	-11.2	-10.9	-10.7	-9.3	-8.5	-6.9	-5.7	-5.5	-5.1	-4.5
$La(OH)_{3(am)}$	-15.9	-15.6	-15.4	-14.1	-13.2	-11.6	-10.3	-10.1	-9.5	-8.2
$Ce(OH)_{3(am)}$	-13.6	-13.4	-13.2	-11.8	-11.0	-9.3	-8.1	-8.0	-7.5	-6.3
$Pr(OH)_{3(am)}$	-13.5	-13.2	-13.0	-11.7	-10.8	-9.2	-8.0	-7.8	-7.4	-6.7
$Nd(OH)_{3(am)}$	-12.9	-12.6	-12.4	-11.1	-10.2	-8.6	-7.5	-7.3	-6.9	-5.9
$Sm(OH)_{3(am)}$	-11.0	-10.7	-10.5	-9.2	-8.4	-6.8	-5.6	-5.6	-5.2	-4.6
$Gd(OH)_{3(am)}$	-10.5	-10.2	-10.0	-8.6	-7.8	-6.2	-5.0	-4.9	-4.5	-3.9
$Tb(OH)_{3(am)}$	-11.3	-11.0	-10.8	-9.4	-8.6	-7.0	-5.9	-5.8	-5.4	-5.0
$Dy(OH)_{3(am)}$	-10.0	-9.7	-9.5	-8.1	-7.2	-5.6	-4.5	-4.5	-4.1	-3.5
$Ho(OH)_{3(am)}$	-10.3	-10.0	-9.7	-8.4	-7.6	-6.0	-4.9	-4.7	-4.4	-4.2
$Er(OH)_{3(am)}$	-11.5	-11.2	-10.9	-9.6	-8.8	-7.1	-6.0	-6.0	-5.6	-5.2
$Tm(OH)_{3(am)}$	-9.7	-9.4	-9.2	-7.9	-7.1	-5.5	-4.4	-4.3	-4.0	-3.9
$Yb(OH)_{3(am)}$	-11.4	-11.1	-10.9	-9.6	-8.7	-7.1	-6.1	-6.1	-5.8	-5.4
$Lu(OH)_{3(am)}$	-11.5	-11.1	-10.9	-9.6	-8.8	-7.2	-6.1	-6.1	-5.8	-5.7
$Y(OH)_3$	-9.7	-9.4	-9.2	-7.8	-7.0	-5.4	-4.2	-4.0	-3.6	-3.0
$La(OH)_3$	-12.7	-12.4	-12.2	-10.9	-10.0	-8.4	-7.1	-6.9	-6.3	-5.0
$Ce(OH)_3$	-12.3	-12.1	-11.9	-10.5	-9.7	-8.0	-6.8	-6.7	-6.2	-5.0
$Pr(OH)_3$	-12.0	-11.7	-11.5	-10.2	-9.3	-7.7	-6.5	-6.3	-5.9	-5.2
$Nd(OH)_3$	-10.5	-10.2	-10.0	-8.7	-7.8	-6.2	-5.1	-4.9	-4.5	-3.5
$Sm(OH)_3$	-8.9	-8.6	-8.4	-7.1	-6.3	-4.7	-3.5	-3.5	-3.1	-2.5
$Eu(OH)_3$	-7.8	-7.5	-7.3	-6.0	-5.1	-3.5	-2.4	-2.3	-2.0	-1.4
$Gd(OH)_3$	-8.1	-7.8	-7.6	-6.2	-5.4	-3.8	-2.6	-2.5	-2.1	-1.5
$Tb(OH)_3$	-8.2	-7.9	-7.7	-6.3	-5.5	-3.9	-2.8	-2.7	-2.3	-1.9
$Dy(OH)_3$	-8.4	-8.1	-7.9	-6.5	-5.6	-4.0	-2.9	-2.9	-2.5	-1.9
$Ho(OH)_3$	-7.9	-7.6	-7.3	-6.0	-5.2	-3.6	-2.5	-2.3	-2.0	-1.8
$Er(OH)_3$	-7.5	-7.2	-6.9	-5.6	-4.8	-3.1	-2.0	-2.0	-1.6	-1.2
$Tm(OH)_3$	-7.4	-7.1	-6.9	-5.6	-4.8	-3.2	-2.1	-2.0	-1.7	-1.6
$Yb(OH)_3$	-7.1	-6.8	-6.6	-5.3	-4.4	-2.8	-1.8	-1.8	-1.5	-1.1
$Lu(OH)_3$	-7.0	-6.6	-6.4	-5.1	-4.3	-2.7	-1.6	-1.6	-1.3	-1.2
$Sc(OH)_3$	-4.7	-4.4	-4.4	-3.7	-3.4	-2.9	-3.1	-3.0	-3.7	-3.2

Table SI-4. Sorbed fraction calculated with data from the experiments with a 0.25 g/L solid:liquid ratio and 20 mM SO_4 in solution.

	Sorbed fraction from experiments with 0.25g/L ratio and 20 mM SO_4 in solution														
pH	**Sc**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
4.74	0.21	0.02	0.01	0.02	0.02	0.03	0.05	0.06	0.07	0.07	0.02	0.01	0.00	-0.02	0.00	0.02
4.89	0.25	0.02	0.01	0.04	0.05	0.05	0.05	0.07	0.08	0.05	0.03	0.02	0.01	-0.04	0.00	0.02
5.17	0.53	0.04	0.01	0.04	0.05	0.05	0.05	0.09	0.07	0.05	0.05	0.02	0.01	0.00	0.02	0.02
5.20	0.43	0.05	0.01	0.07	0.05	0.08	0.07	0.09	0.09	0.04	0.05	0.03	0.01	0.00	-0.01	0.03
5.42	0.66	0.06	0.03	0.08	0.06	0.06	0.08	0.10	0.09	0.09	0.04	0.04	0.03	0.00	0.04	0.04
5.63	0.80	0.11	0.02	0.10	0.09	0.08	0.10	0.10	0.07	0.09	0.02	0.04	0.06	0.04	0.05	0.06
5.81	0.85	0.14	0.05	0.12	0.09	0.12	0.14	0.13	0.12	0.11	0.10	0.09	0.09	0.12	0.13	0.15
5.92	0.91	0.16	0.07	0.15	0.15	0.16	0.17	0.17	0.14	0.16	0.13	0.14	0.09	0.13	0.18	0.16
6.05	0.93	0.22	0.08	0.21	0.17	0.19	0.24	0.24	0.21	0.22	0.22	0.20	0.21	0.25	0.31	0.29

Table SI-5. Experimental log K_D (L/Kg) from experiment with 20 mM SO_4 and 0.5 mM SO_4, respectively.

	log K_D																
	experiment with 20 mM SO_4																
pH	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	K_D^Y/K_D^{Dy}	K_D^Y/K_D^{Ho}
4.34	2.75	-	1.14	0.84	0.90	1.11	1.14	1.24	1.21	1.07	1.24	1.26	1.26	1.24	1.41	1.26	-	-
4.45	2.92	-	1.28	1.40	1.30	1.40	1.47	1.44	1.44	1.46	1.54	1.52	0.00	1.59	1.71	1.61	-	-
4.48	2.86	-	1.41	1.38	1.28	1.43	1.46	1.45	1.48	1.33	1.49	1.45	0.00	1.41	1.51	1.39	-	-
4.88	3.66	1.70	1.74	1.77	1.81	1.83	1.87	1.85	1.90	1.85	1.94	1.88	0.00	1.98	2.09	2.02	0.58	0.66
4.94	3.92	1.96	-	2.00	2.00	2.03	2.10	2.07	2.06	2.07	2.13	2.11	1.51	2.20	2.32	2.28	0.66	0.70
5.46	5.11	2.48	1.71	1.89	2.36	2.40	2.55	2.41	2.50	2.59	2.67	2.64	2.57	2.80	2.95	2.91	0.65	0.69
5.74	5.65	2.67	1.99	2.14	2.51	2.56	2.72	2.63	2.65	2.77	2.86	2.82	2.81	3.01	3.16	3.12	0.64	0.70
6.06	5.95	3.13	2.38	2.71	2.89	2.97	3.17	3.15	3.10	3.19	3.33	3.26	3.33	3.47	3.65	3.60	0.64	0.74
6.22	5.95	3.27	2.72	2.95	3.05	3.14	3.32	3.30	3.25	3.34	3.45	3.40	3.45	3.59	3.75	3.71	0.66	0.75
6.51	5.94	3.78	3.14	3.40	3.53	3.61	3.82	3.82	3.74	3.88	3.97	3.94	3.99	4.14	4.29	4.27	0.64	0.69
6.85	5.94	4.01	3.46	3.68	3.80	3.86	4.05	4.05	3.98	4.10	4.19	4.15	4.21	4.34	4.48	4.48	0.66	0.71
	experiment with 0.5 mM SO_4																
pH	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	K_D^Y/K_D^{Dy}	K_D^Y/K_D^{Ho}
4.36	2.19	1.00	1.00	1.33	1.00	1.26	1.31	1.09	1.51	1.20	1.00	1.29	1.31	1.29	1.00	1.05	1.00	0.52
4.47	2.28	1.17	1.00	1.34	1.05	1.13	1.34	1.09	1.00	1.29	1.00	1.00	1.00	1.00	1.00	1.05	1.47	1.47
4.54	2.70	1.23	1.05	1.40	1.17	1.00	1.00	1.13	1.40	1.34	1.00	1.00	1.00	1.00	1.00	1.05	1.69	1.69
5.00	3.48	1.26	1.41	1.59	1.46	1.62	1.73	1.67	1.77	1.71	1.09	1.72	1.78	1.83	1.00	1.90	1.47	0.35
5.31	3.90	1.95	1.88	2.00	1.96	2.07	2.13	2.14	2.24	2.15	1.86	2.16	2.20	2.26	2.12	2.31	1.22	0.62
5.88	4.27	2.44	2.22	2.30	2.31	2.35	2.44	2.45	2.48	2.46	2.33	2.47	2.37	2.55	2.50	2.77	1.29	0.93
6.35	4.89	2.85	2.49	2.69	2.86	2.95	3.04	3.00	2.99	3.05	3.03	3.06	3.06	3.16	3.20	3.22	0.66	0.63
6.52	4.91	3.25	2.94	3.17	3.22	3.29	3.47	3.47	3.38	3.46	3.50	3.46	3.51	3.58	3.69	3.68	0.57	0.62
6.75	5.64	3.58	3.20	3.45	3.58	3.67	3.89	3.88	3.77	3.86	3.86	3.85	3.87	3.97	4.04	4.06	0.52	0.54
8.40	5.33	5.62	5.62	5.62	5.90	5.60	5.90	5.90	5.89	5.90	5.61	5.89	5.62	5.90	5.61	5.90	1.01	0.53

Table SI-6. REE surface complexation constants for aqueous carbonate complexes estimated from values obtained by Quinn et al., 2006 b (table2).

Element	Surface Complex	Log K_M^{CO3}	Error	Log $K_{M(CO3)}$ - 1.75	Error
Y	$XOYCO_3$	-1.30		-3.05	-
La	$XOLaCO_3$	-0.39		-2.14	-
Ce	$XOCeCO_3$	-0.21		-1.96	-
Pr	$XOPrCO_3$	-0.22		-1.97	-
Nd	$XONdCO_3$	-0.20		-1.95	-
Sm	$XOSmCO_3$	-0.20		-1.95	-
Eu	$XOEuCO_3$	-0.26		-2.01	-
Gd	$XOGdCO_3$	-0.38		-2.13	-
Tb	$XOTbCO_3$	-0.40		-2.15	-
Dy	$XODyCO_3$	-0.51		-2.26	-
Ho	$XOHoCO_3$	-0.57		-2.32	-
Er	$XOErCO_3$	-0.59		-2.34	-
Tm	$XOTmCO_3$	-0.56		-2.31	-
Yb	$XOYbCO_3$	-0.62		-2.37	-
Lu	$XOLuCO_3$	-0.59		-2.34	-

Fig. SI-1 X-ray Diffraction Pattern for synthetic basaluminite previous to sorption experiments (pure) and basaluminite after REE adsorption with sulfate presence at four different pH values obtained at ID-31 beamline, ESRF. The peaks observed are artifacts due to the panel detector (see Lozano et al., 2018 for details).

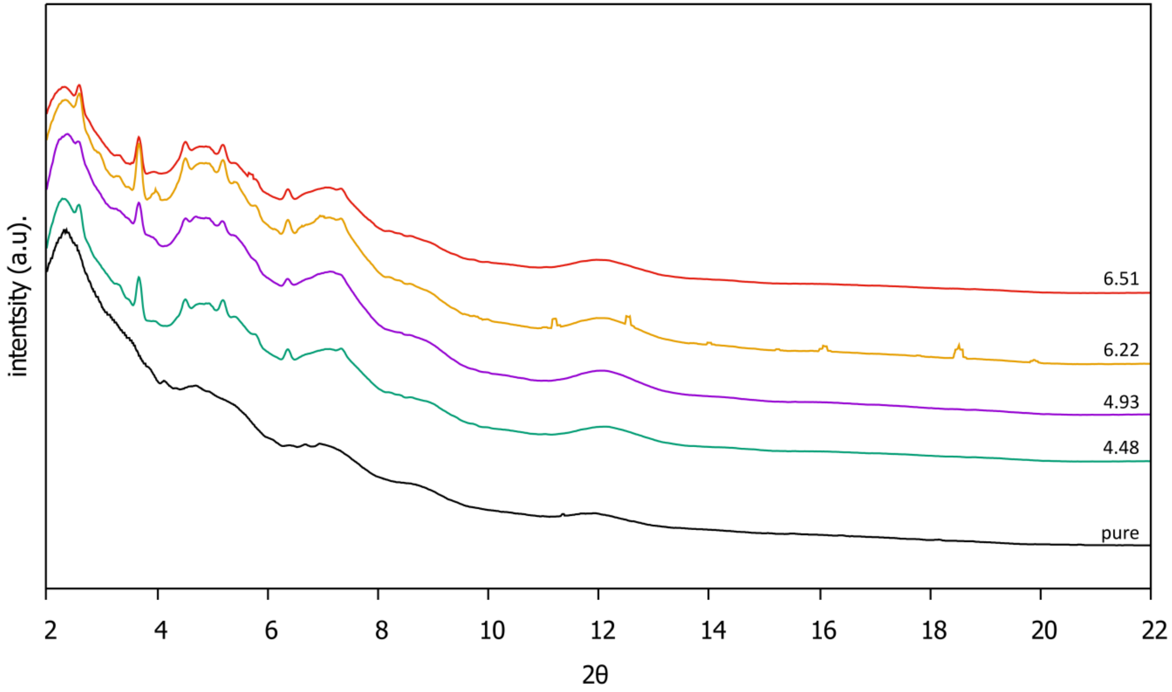


Fig. SI-2. Distribution of the surface sites in basaluminite structure.

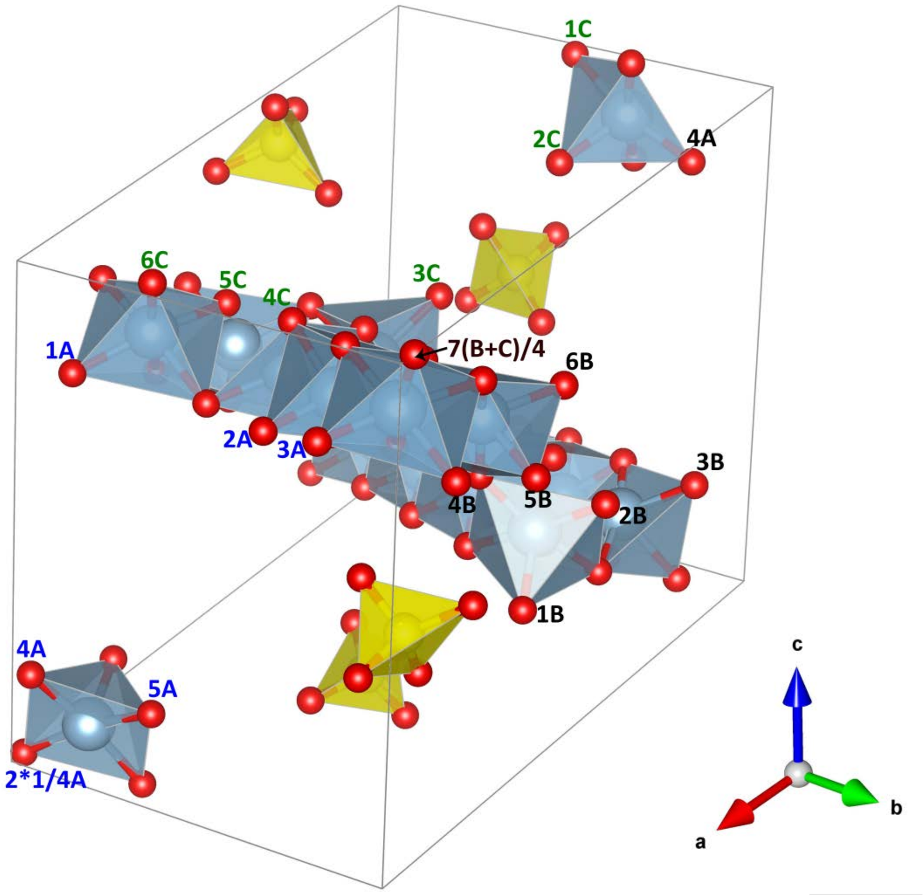


Fig. SI-3. Predictions of REE adsorption in experiment with 20 mM sulfate using surface complexation constants in table 2.

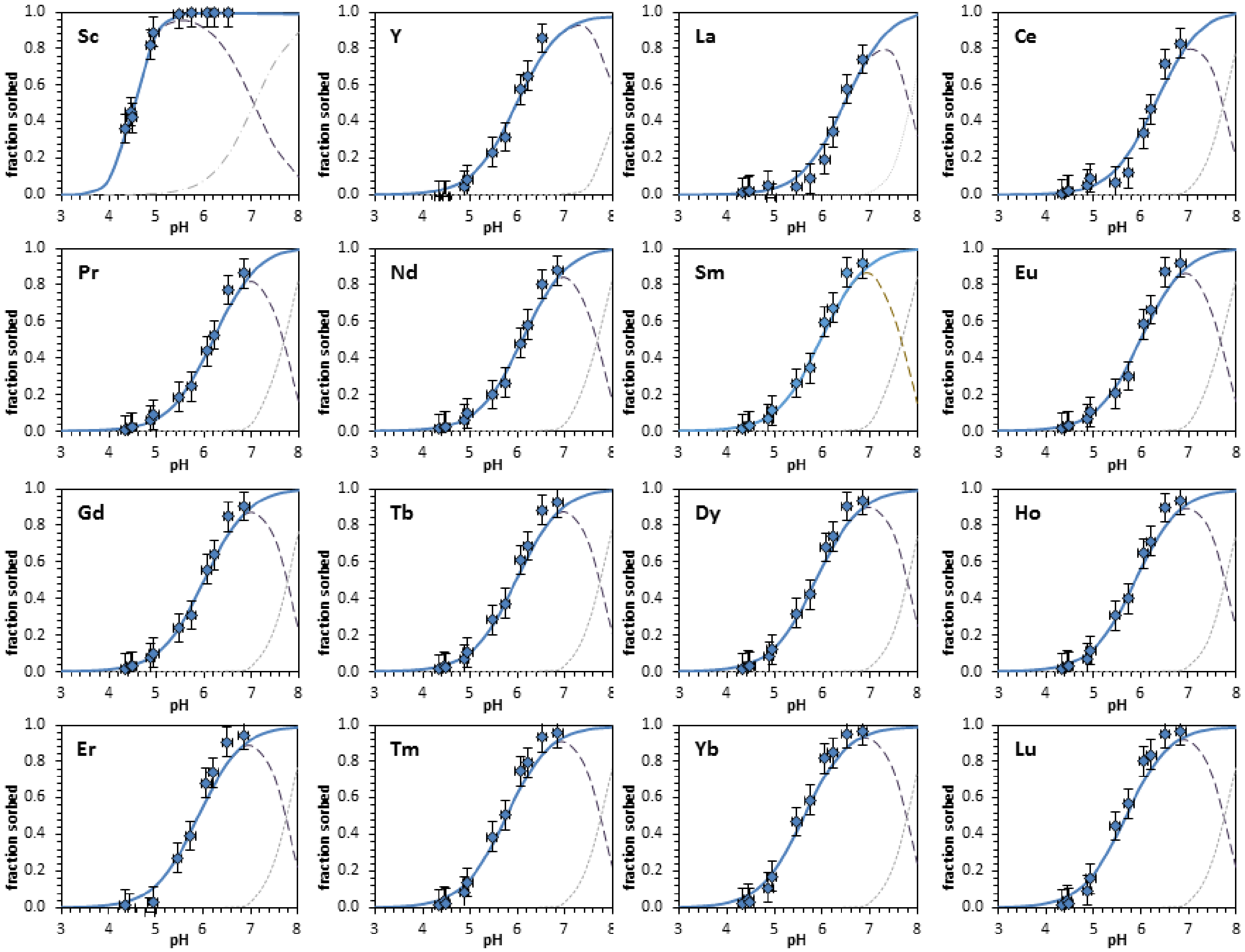


Fig SI-4. Predictions of REE adsorption in experiment with 0.5 mM sulfate using surface complexation constants in table 2.

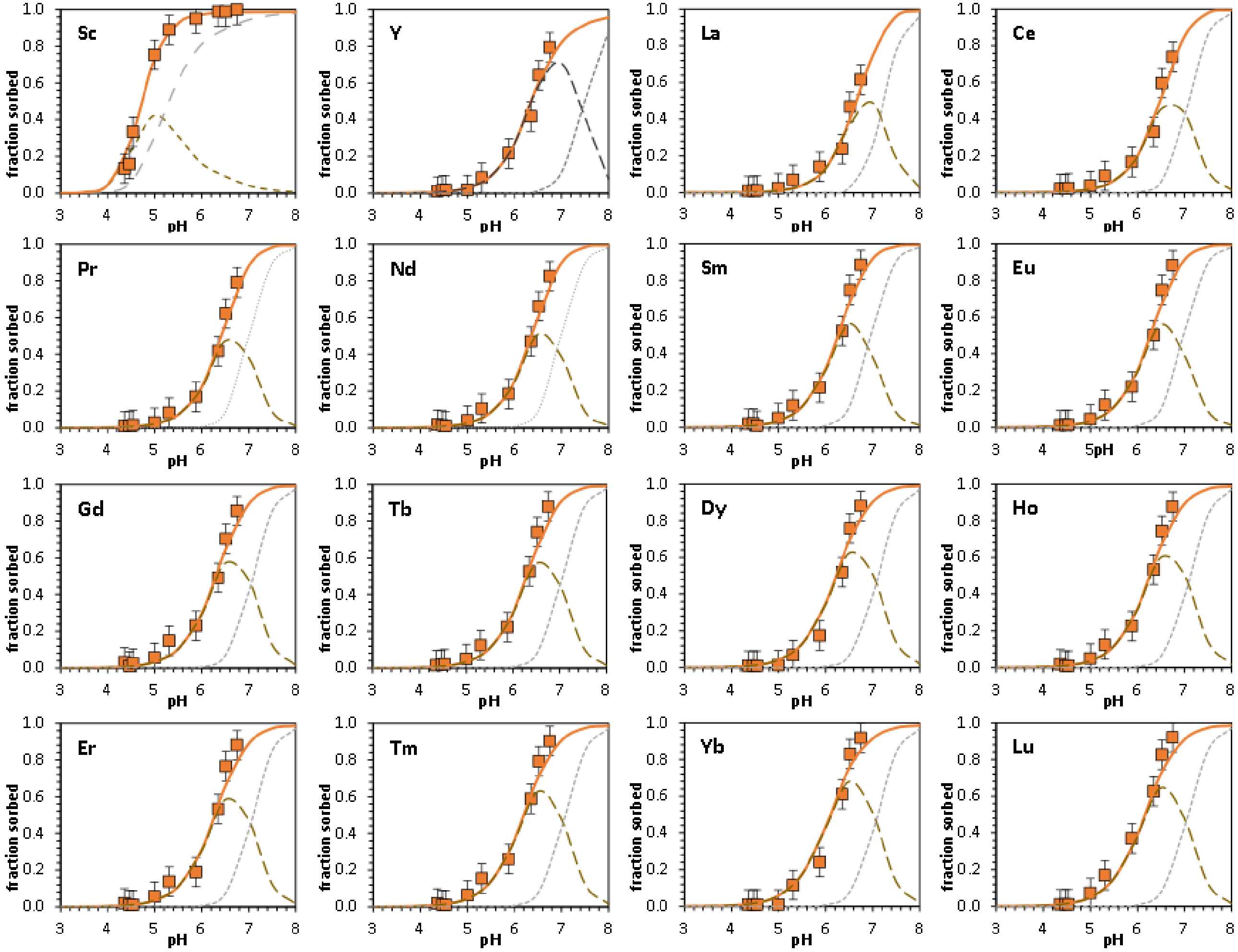


Fig. SI-5. Experimental data (symbols) and model (lines) of fractionation constants (log K_D) for lanthanide series in (A) sorption experiment without 20 mM sulfate and (B) with 0.5 mM sulfate. Calculations at 25 C and pCO$_2$ of 3.5 including sorption of both MSO_4^+ and MCO_3^+ aqueous species. Log K_D^{Sc*} represents Log K_D^{Sc}-2

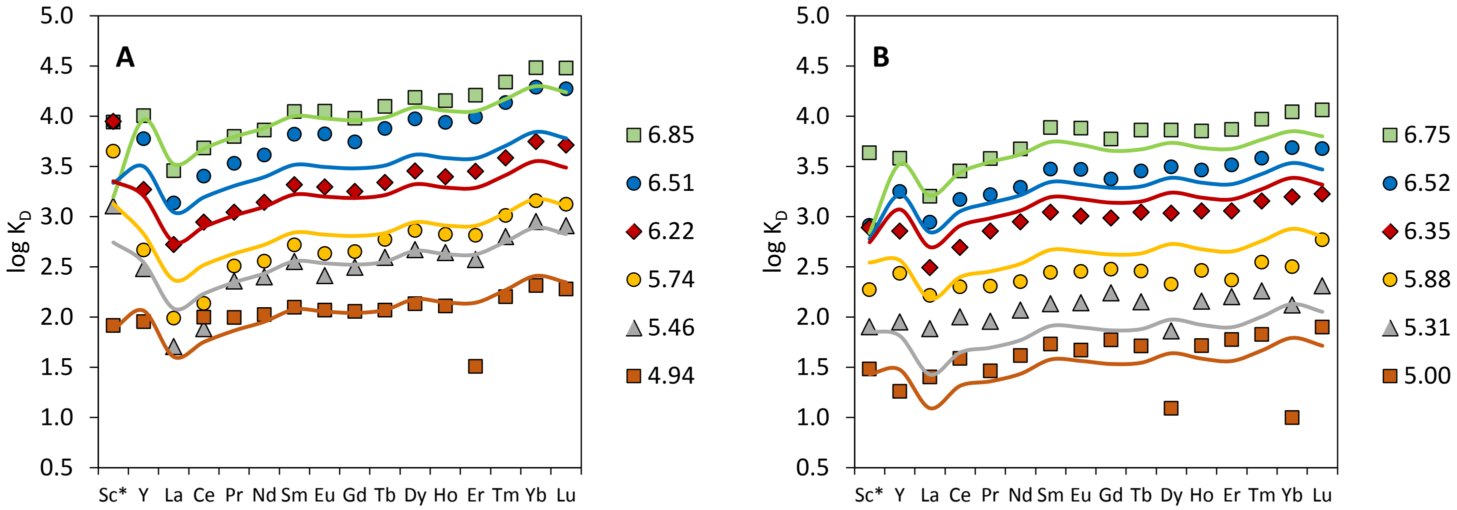
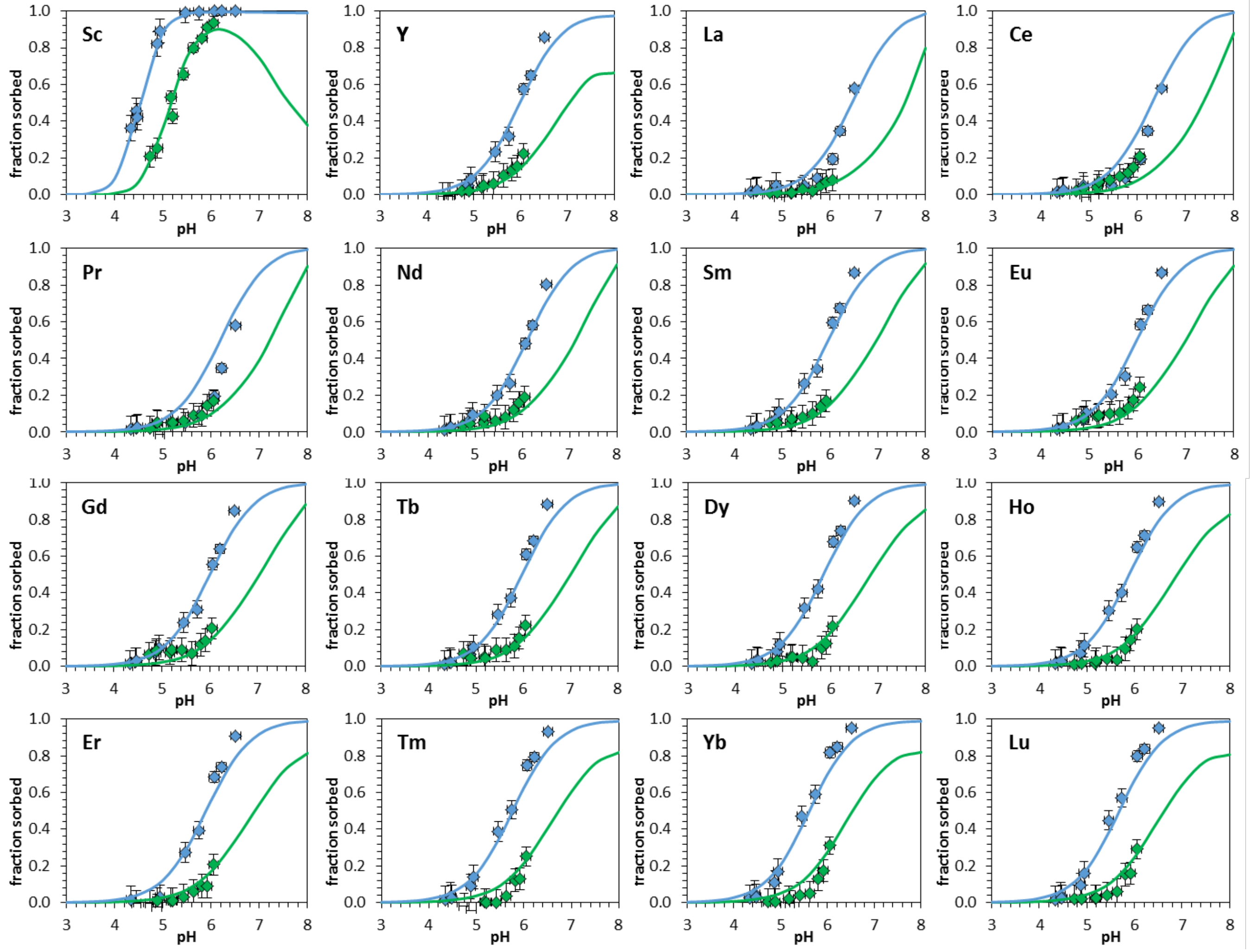


Fig SI-6. REE sorption fraction for two different solid:solute ratios 1 g/L (blue), 0.25 g/L (green) obtained from experimental data (symbols) and the predicted model for each experiment (lines).



Article 3

Sorption of rare earth elements on schwertmannite and their mobility in acid mine drainage treatments

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Sorption of rare earth elements on schwertmannite and their mobility in acid mine drainage treatments

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Abstract

Rare Earth Elements (REE) are nowadays considered critical raw materials due to their increasing use in modern and their shortage of supply. Acid mine drainage (AMD) contains REE concentrations several orders of magnitude higher than the rest of continental and marine waters, and the sludge from its treatment may become a supplementary source of REE. Schwertmannite, a Fe(III)-sulfate-hydroxide is the most common mineral precipitated from AMD and a main constituent of the neutralization sludge. The objective of this work is to study the mechanism of REE retention in schwertmannite.

Suspensions of synthetic schwertmannite in sulfate solutions showed that Y and the lanthanides are effectively sorbed at pH values higher than 4.5, and sorption is complete at pH values higher than 6.5. The experimental partition coefficients clearly show a preferential enrichment of heavy REE in the solid phase. Unlike the rest of the REE, Sc sorption occurred at a lower pH, from 3 to 5. The experimental results have been described with a non-electrostatic surface complexation model in which the aqueous complex MSO_4^+ exchanges with two H^+ from the surface of schwertmannite, forming a bidentate surface complex, $(XO)_2MSO_4^-$. Scandium sorption was also accurately predicted with the addition of a second bidentate surface complex, $(XO)_2MOH$.

The model was applied to describe the behavior of different REE observed in the pore water and solid of a column experiment imitating a scaled AMD passive remediation system. Both basaluminite and schwertmannite were the main solid phases formed. Although both minerals have similar sorption edges, Y and the lanthanides sorbed at pH values higher than 4.5, and sorption only occurred on basaluminite because schwertmannite formed at a pH below 4. In contrast, the Sc sorption edge extended from pH 3 to 5 and, therefore, it partially sorbed on schwertmannite. As a practical consequence, REE preferentially accumulated in the basaluminite residue of AMD neutralization systems, but a significant fraction of Sc can be retained in the schwertmannite waste.

Keywords

Scandium, yttrium, lanthanides, non-electrostatic model, bidentate surface complex, passive remediation, neutralization sludge

Highlights

- Sorption of REE on schwertmannite highly depends on pH
- Sorption affinity for schwertmannite increases from LREE to HREE and particularly to Sc
- In AMD treatment plants a fraction of sorbed Sc accumulates in the schwertmannite sludge
- Sc can be segregated from the rest of REE by keeping the neutralization pH below 4.5
- A sorption model predicts the REE mobility in acid water treatments

1 Introduction

The rare earth elements (REE) form the largest chemically coherent group in the periodic table. According to the International Union of Pure and Applied Chemistry, it is formed by the lanthanide series, yttrium and scandium. Their similar atomic structure and chemical properties as well as the small differences among the elements in the group have traditionally converted their partition between water and minerals as tracers of geochemical processes (Henderson, 1984; McLennan, 1989; Elderfield et al., 1990, among many others). Beyond their importance as geochemical tracers, in the last two decades, it has been an increasing interest in REE due to their higher demand by modern technology and industry. This demand, together with eventual shortages of supply has motivated the search for alternative sources of REE raw material worldwide (Hatch, 2012; Massari and Ruberti, 2013).

On the other hand, Acid Mine Drainage (AMD) is one of the most important and spread pollution affecting watersheds and ecosystems (Nordstrom et al., 2015). However, AMD could also become a new and supplementary source for REE since their concentration in AMD, including scandium, is two to three orders of magnitude higher than in natural waters (Noack et al., 2014). In AMD, pH has been described as the key factor for REE mobility. Thus, the pH increase to circumneutral values when AMD mixes with alkaline waters leads to the precipitation of hydrous ferric/aluminum oxides and sulfate-hydroxides, accompanied with the REE scavenge (Verplanck et al. 2004; Gammons et al., 2005 a, b; Ferreira da Silva et al., 2009).

In addition to REE, AMD also contains high concentrations of toxic elements, and represents a very important environmental threat that requires remediation. In mine operations, the active treatments of AMD are mainly based on its neutralization with alkaline reagents, usually limestone, sodium carbonate or ammonia (Evangelou and Zhang, 1995; Coulton et al., 2003). This treatment produces high amounts of an sludge formed by a mixture of Fe(III) and Al-sulfate-hydroxides which disposal represents a major operating cost for the companies and an environmental concern (Ackman, 1982; Viadero et al., 2006). Differently, the passive remediation systems neutralize the AMD by driving it through a permeable system filled with grained limestone (Heding et al., 1994; Cravotta and Trahan, 1999; Ayora et al., 2013). Along the process, the waste created is represented by a sequential precipitation of mainly schwertmannite ($Fe_8O_8(OH)_6SO_4$ and basaluminite ($Al_4SO_4(OH)_{10}\cdot 5H_2O$). Moreover, REE have been proved to be entirely retained in the solid waste resulting from AMD treatment with REE_2O_3 rates comparable to present day exploitations and prospects (Ayora et al., 2016; Zhang and Honaker, 2018). This study did not include Sc, which market value is one and two orders of magnitude higher than that of Heavy and Light REE, respectively (USGS, 2019). The retention of REEs on basaluminite and the dependence of this process on pH and sulfate availability has already been studied (Lozano et al., 2019). However, despite the overwhelming presence as precipitates in AMD streams (Nordstrom, 2011), and being the other major constituent of AMD treatment sludge, the interaction between schwertmannite and REEs remains unknown.

Previous laboratory experiments of sorption and coprecipitation of REE onto ferric and manganese oxides/hydroxides have previously demonstrated the key role of pH in the geochemical mobility of REE (De Carlo et al., 1998; Bau 1999; Ohta and Kawabe 2000, 2001; Quinn et al., 2004, 2006a). REE are removed from solution as the pH increases from 4 to 9. In addition to pH, aqueous speciation is also an important factor that has been driven its attention in REE fractionation in marine environments. Thus, the formation of strong carbonate complexes with heavy REE (HREE) at neutral pH values prevents their sorption by ferric and manganese oxides. As a result, these solids show patterns with light REE (LREE) enrichment (Byrne and Kim, 1990; Koeppenkastrop and De Carlo, 1992; Sholkovitz, 1995; Byrne and Sholkovitz, 1996; Kawabe et al., 1999a,b). More recently, some works have performed detailed sorption experiments and developed surface complexation models to describe the sorption of some lanthanides (Yb, La, Eu) onto hematite and amorphous ferric oxides/hydroxides (Marmier et al., 1997; Rabung et al., 1998; Marmier and Fromage, 1999; Quinn et al., 2006a,b; Estes et al., 2013; Liu, 2017). In these works, the REE scavenging is mainly explained by the sorption of free REE ions or their hydrolyzed species onto a solid surface.

The presence of sulfate is ubiquitous in AMD systems, usually with concentrations reaching up to several grams per liter. Rather than free ions or hydrolysis products, previous studies have highlighted the importance of aqueous sulfate complexes with REEs (Gimeno et al., 2000; Verplanck et al., 2004). Similar to REE-carbonate speciation in seawater, sulfate complexes may explain REE fractionation in the solids precipitated from AMD environments. Therefore, due to its importance in AMD chemistry, the role of sulfate in REE sorption on schwertmannite must be quantitatively assessed.

Here, we present the results from REE sorption experiments on synthetic schwertmannite in an AMD setting. A non-electrostatic surface complexation model is developed to describe the experimental data for the sorption of a complete data set of REE (lanthanides, Y and Sc) at different pH values, sulfate concentrations and solid:liquid ratios. The model is then used to interpret the mobility of the different REE in a column experiment reproducing a scaled AMD passive treatment system.

2 Materials and methods

2.1 Experimental techniques

2.1.1 Structural characterization of synthetic schwertmannite

Synthetic schwertmannite was prepared following the procedure described by Cornell and Schwertmann (1996), where 10.8 g of $FeCl_3 \cdot 6H_2O$ and 3 g of Na_2SO_4 were mixed with 2 L of distilled water at 60°C. The suspension was stirred for 12 minutes at 60°C and then cooled to room temperature. The solid was dialyzed in a cellulose membrane against double-distilled water for 33 days. Once the water had conductivity less than 0.5 mS/cm, the precipitate was freeze-dried. Mineral purity was assessed by X-ray diffraction (XRD). The specific surface area was measured by the BET-N_2 sorption method (Micromeritics Gemini V analyzer; Micromeritics.

2.1.2 REE sorption as a function of pH and sulfate concentration

The REE sorption on synthetic schwertmannite was measured as a function of pH at two different sulfate concentrations in two separate sets of batch experiments using suspensions of 1 g/L. Two stock solutions with a pH of 2.5 were prepared for each set. The first stock solution consisted of REEs at a concentration of 1 mg/L each and 20 mM SO_4, whereas the second stock solution consisted of REEs at a concentration of 1 mg/L each and 2 mM SO_4. The solutions were prepared with an ICP standard mix of 16 elements, excluding Pm, and Na_2SO_4 (ACS reagent >99.9%, Merck). The stock solutions were intended to simulate acid mine waters with different sulfate concentrations. First, 10-mL aliquots of each stock solution were transferred to 50-mL centrifuge tubes, and the pH of each aliquot was adjusted to cover a pH range of 3-7 by adding small amounts of a 0.05 M NH_4OH solution. After adding 10 mg of schwertmannite to each aliquot, the suspensions were shaken for 6 hours at room temperature. Then, the suspensions were centrifuged for 15 minutes at 4500 rpm (4150 RCF), and the supernatant was filtered through 0.22-µm nylon membranes and transferred to test tubes diluted fivefold with 1% HNO_3. The solids were dried at 40°C for 48 hours. The sorbed fractions were calculated as follows:

$$\text{Sorbed fraction} = \frac{[\mathrm{REE}]_{\mathrm{initial}} - [\mathrm{REE}]_{\mathrm{final}}}{[\mathrm{REE}]_{\mathrm{initial}}} \qquad (1)$$

where [REE] is the concentration of each REE. The initial concentration was measured in the stock solution and the final concentration after the experiment. The distribution coefficient, K_D (L/kg), for each REE was calculated from the [REE] sorbed onto the solid per the final [REE] remaining in solution and normalized per the solid:liquid ratio:

$$\mathrm{K_D} = \frac{[\mathrm{REE}]_{\mathrm{initial}} - [\mathrm{REE}]_{\mathrm{final}}}{[\mathrm{REE}]_{\mathrm{final}}} \cdot \frac{\mathrm{V_{solution}}}{\mathrm{M_{solid}}} \qquad (2)$$

2.1.3 Description of the column experiment and waste characterization

To obtain a vertical profile of REE distribution in the pore water and in the minerals precipitated along the passive AMD remediation system designed for the Poderosa mine (SW Spain), a scaled column experiment was carried out. The column was built with transparent polymethyl methacrylate (9.6-cm inner diameter and 35 cm in height). A 3-cm layer of glass beads (3 mm in diameter) and a perforated drainpipe were installed at the bottom of the column. Lateral ports located at 3-cm intervals in the upper part of the column allowed pore water sampling. The column was filled with 20 cm of dispersed alkaline substrate consisting of 30 g of limestone sand (0.5-1 mm) and 300 g of pine-wood shavings (5-10 mm) (Rötting et al., 2008a). The role of the pine-wood shavings was to provide a porous matrix to allocate the minerals that precipitated inside the column and prevent clogging. The proportion of limestone was decided to be small in order to exhaust the reagent within a few weeks. The initial total porosity of the filling was 0.46, determined by a gravimetric method.

The column was open to the atmosphere, and the input AMD was pumped into the top of the column with a peristaltic pump. The water flowed downward by gravity through the limestone substrate at a constant flow rate of 3.5 mL/min. This flow was similar to that of 2 L/s, which is the flow rate expected for a field-scale treatment of 200 m^2 of surface area to treat the discharge of the Poderosa mine. Water samples were collected every week from the supernatant, and 3 sampling points at 4, 7, 10 and 23 cm depth. No pore water could be sampled between 10 and 23 cm. For each water sample, pH, redox potential, electrical conductivity, oxygen concentration and total alkalinity were measured in situ. The water was filtered through 0.22-µm nylon filters and stored at 4°C until analysis. The experiment lasted for 58 days and was stopped when the outflow showed a pH lower than 5.5, as an indication of reagent efficiency exhaustion.

Postmortem, the column was drained, and the residue was divided into 2-cm slices and dried at room temperature. The major mineral phases present in the solid residue were identified by XRD. To investigate the partitioning of Al, Fe, and trace elements into the solid phases, a sequential extraction procedure adapted from Torres and Auleda (2013) was applied to the residue samples to obtain the following fractions: 1) the water-soluble fraction, extracted with deionized water; 2) calcite and basaluminite, extracted with 1 M ammonium acetate at pH 4; 3) low crystalline Fe(III)-oxyhydroxides and remaining basaluminite, extracted with 0.2 M ammonium oxalate at pH 3; 4) crystalline Fe(III)-oxides, extracted with 0.2 M ammonium oxalate at pH 3 in a water bath at 80°C for 2 hours; and 5) the residual fraction, extracted with concentrated $HClO_4$ and HNO_3 at 135°C. All the leachates resulting from the different extraction steps were filtered through 0.22-µm nylon syringe filters and stored at 4°C until analysis. Duplicates for 10% of the total samples were analyzed, showing a reproducibility of 90%. To validate the sequential extraction procedure, a total digestion (performed according to step 5 of the protocol) of all the samples was conducted. The addition of sequential extractions was compared with the total extraction from the digestion, and only element recovery rates between 80% and 120% were accepted.

2.2 Analytical techniques

Measurements of pH from filtered aliquots were made with a Crison® glass electrode calibrated with buffer solutions of pH 2, 4, 7 and 9. Major cations were measured by ICP-AES (Thermo Scientific – iCAP 6500, radial acquisition), and REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y and Sc) were measured with ICP-MS (Perkin-Elmer®SciexElan 6000). The detection limits were 0.2 µg/L for REEs and 0.1, 0.05, 0.1 and 0.1 mg/L for S, Fe, Al and Na, respectively. The analytical precision error was estimated to be approximately 2% for ICP-MS and ICP-AES measurements. Certified solutions (CPI International-CCV standard 1-solution A) were intercalated within the samples to check the analytical accuracy. Two AMD laboratory standards supplied by P. Verplank (USGS) were also analyzed for REE accuracy, yielding deviations lower than 4% of the recommended values, with the exception of Eu, which showed values 19% below the recommended value (Verplanck et al., 2001).

The XRD patterns of the solid phases after the experiments were obtained using a Bruker D8 A25 Advance Diffractometer θ-θ with CuKα1 radiation. The diffractometer operated at 40 kV and 40 mA in a Bragg-Brentano geometry and was equipped with a linear LynxEye XE detector. The diffractograms were obtained from 4° to 60° in 2θ with a step size of 0.015° and a counting time of 0.1 s.

2.3 Geochemical modeling

Chemical speciation of dissolved REE, saturation indexes of solid phases, surface complexation and 1D reactive transport modeling were calculated with the PHREEQC code (Parkhurst and Appelo, 1999) using the database Donnee Thermoddem_V1.10.dat (Blanc et al., 2012). The database has been updated with the stability constants at zero ionic strength and 25°C for the following inorganic complexes for the lanthanides and yttrium (M): MCO_3^{+}, MCO_3^{-2}, $MHCO_3^{+2}$ (Luo and Byrne, 2004); MSO_4^{+} (Schijf and Byrne, 2004); MOH^{+2} (Klungness and Byrne, 2000); MOH_2^{+}, MOH_3 (Lee and Byrne, 1992); MCl^{+2} (Luo and Byrne, 2001); MF^{+2}, MF_2^{+} (Luo and Millero, 2004); and MNO_3^{+2} (Millero, 1992). Solubility products for REE $M(OH)_3$ and $M(OH)_{3(am)}$ solids have been complementarily loaded from the LLNL database (Johnson et al., 1992) and

Spahiu and Bruno (1995). Scandium aqueous complexes, $Sc(OH)^{+2}$, $Sc(OH)_2^+$, $Sc(OH)_3$, and $ScSO_4^+$, and the solubility product for $Sc(OH)_3$ by Wood and Samson (2006) were incorporated. The reactions and their equilibrium constants are compiled in Table S1 of the Supplementary Information. The solubility products of schwertmannite and basaluminite were obtained from Sanchez-España et al. (2011).

The reactive transport model consisted of 20 cm of calcite followed by 5 cm of an inert matrix of glass beads. An initial concentration of 0.25 mol/L of calcite was percolated by an inflow of AMD. As the acid water infiltrates, calcite dissolves according to the kinetic law described by Plummer et al. (1979) and included in the database of the PHREEQC code. The rest of minerals, schwertmannite, basaluminite and gypsum were assumed to precipitate in equilibrium. The reactive surface area of calcite was calibrated to 0.23 m^2/L in order to fit the observed pH profiles. The surface complexes and log K values described in Table 1 were used to describe the Sc sorption on schwertmannite, and those of Lozano et al. (2019) were used to calculate the lanthanide and Y sorption onto basaluminite. As initial conditions, the number of sorption sites was deduced from the properties of schwertmannite (4.7 sites/nm^2; 173 m^2/g, as will be described in section 3.1) and basaluminite (4.6 sites/nm^2, 68 m^2/g according to Lozano et al., 2019). The solid/liquid ratio for both minerals was calculated from their total amount formed, which were calculated in a previous run of the model without sorption reactions distributed in the column, and assuming a bulk solid density of 1.3 kg/L (including the wood shavings) and a porosity of 0.46. The numerical grid was divided into 25 elements of 1 cm each.

3 Results

3.1 Characterization of synthetic schwertmannite

The XRD patterns of the solid phase prior to and after the sorption experiments confirmed that the mineral was pure schwertmannite (Fig. S1, S2). The measured specific surface area of pure schwertmannite was 173 m^2/g, close to the values reported by Antelo et al. (2012) and Regenspurg et al. (2004) (171 m^2/g and 175-200 m^2/g, respectively). The site density was calculated from the crystal structure proposed by Fernández-Martínez et al. (2010), accounting for the single coordinated sites per face area, yielding values of 2 sites/63.22 $Å^2$ for (1 0 0), 7.5 sites/113.77 $Å^2$ for (0 1 0) and 2 sites/64.95 $Å^2$ for (0 0 1) (Fig. S3). These calculations resulted in a total site density of 4.75 sites/nm^2, a value similar to 4.7 sites/nm^2 reported by Fukushi et al. (2004). The resulting total concentration of surface sites was therefore 1367 µmol/g.

3.2 REE sorption as a function of pH and sulfate concentration

Prior to sorption experiments, the kinetics of the sorption reactions were determined using 10 suspensions of 1 g/L schwertmannite and a solution of REE at a concentration of 1 mg/L each and 20 mM SO_4 at pH 5.5. The kinetics experiments showed a very fast initial sorption, which increased until a steady state was reached at 5 hours (Fig. S4). Similar equilibrium times were observed for ferric oxyhydroxide by Ohta and Kawabe (2001) and Koeppenksastrop and De Carlo (1992), with fast REE adsorption at approximately 4-6 hours. Therefore, sorption was considered almost complete after 6 hours of contact during the sorption experiments.

The chemical composition data of the initial and final solutions for the two sets of sorption experiments with 20 and 2 mM SO_4 are compiled in Tables S2 and S3, respectively. All solutions at the end of the sorption experiments were subsaturated with respect to the REE hydroxides (Tables S4, S5), and thus the hydroxide precipitation was discarded. The solutions were also subsaturated with respect to schwertmannite and almost in equilibrium with respect to goethite. Schwertmannite exists in a metastable phase that transforms to goethite over weeks at different pH values (Schwertmann and Carlson, 2005; Acero et al., 2006; Burton et al., 2009). However, the presence of sulfate in solution delays this transformation (Regenspurg and Peiffer, 2005), and goethite was not detected by XRD in schwertmannite solids after the sorption experiments (Fig. S1, S2).

Sorption showed a high dependence on pH in the two sets of experiments, as the REE sorption increased with pH (Fig. 1). The sorption edges occurred within a range of 2.0 to 2.5 pH units and shifted to lower pH values for HREE than for LREE, showing that HREE sorption was favored over LREE sorption at the same pH value. Similar pH dependence was observed by Bau (1999) and Quinn et al. (2006a) in REE coprecipitation with amorphous ferric hydroxide and by Lozano et al. (2019) in REE sorption on basaluminite.

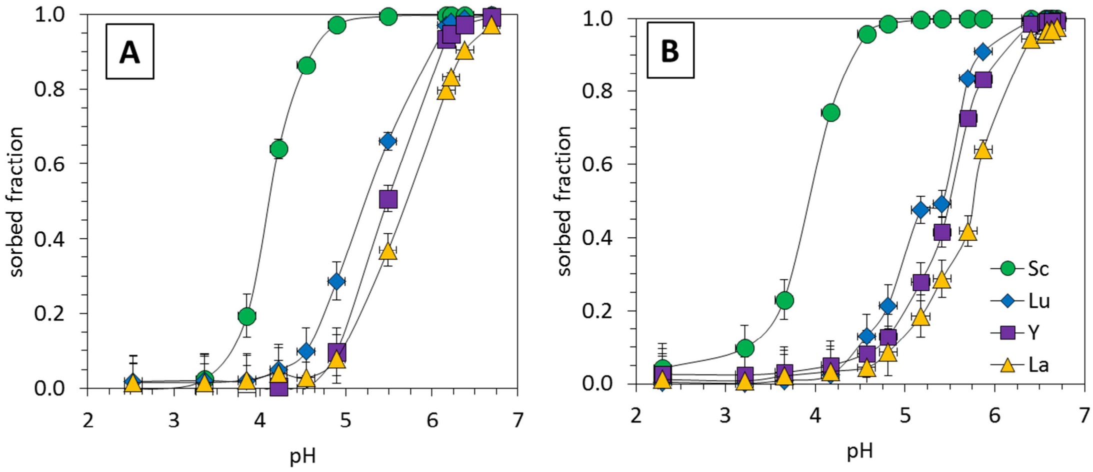

Fig. 1. Sorption edges of selected REE on schwertmannite in solutions with 20 mM (A) and 2 mM (B) sulfate. Legend: Sc: circles, Y: squares, Lu: squares and La: diamonds. The error bars indicate the uncertainties in pH measurements (± 0.02) and in the sorbed fraction (from ±0.01 to ±0.07).

The pH at which sorption becomes significant depends on the element. The lanthanides and Y started to sorb at pH 5, whereas Sc started at pH 3.5, a value considerably lower than the rest of the REE. In the experiment with 20 mM SO_4 at pH 4.9, more than 95% of Sc was adsorbed on schwertmannite, whereas less than 20% of the remaining REE were adsorbed. Similar behavior was also observed for basaluminite (Lozano et al., 2019), although here Sc sorption occurred at a pH lower than 4, at which basaluminite is not stable.

The distribution coefficients (K_D) for both sets of experiments were calculated as described in Eq. (2) and are shown in Fig. 2. The REE fractionation patterns showed four convex segments from La to Nd, from Nd to Gd, from Gd to Ho and from Ho to Lu, corresponding to the M-type tetrad effect (Masuda et al., 1987; Bau et al., 1996). The K_D values increased by 3 orders of magnitude a pH increases from 4.5 to 6.5, highlighting the dependence of REE sorption on pH. At pH values higher than 5, when sorption becomes significant, the K_D values clearly showed an enrichment of HREEs in the solid phase, which increased by 1 order of magnitude along the lanthanide series. Similar REE patterns with HREE enrichments appeared in free REEs that were coprecipitated with synthetic Fe(III)-hydroxides (De Carlo et al., 1998; Quinn et al., 2004). These results contrast with those described in seawater environments, where a preferential LREE enrichment in the Fe oxides has been observed. Stable aqueous carbonate complexes with HREE formed in marine environments to prevent their adsorption (Koeppenkastrop and De Carlo, 1992; Kawabe et al., 1999b). In acid mine waters, however, sulfate complexes are the dominant aqueous species, while carbonate complexes are only relevant at pH values higher than 6.5.

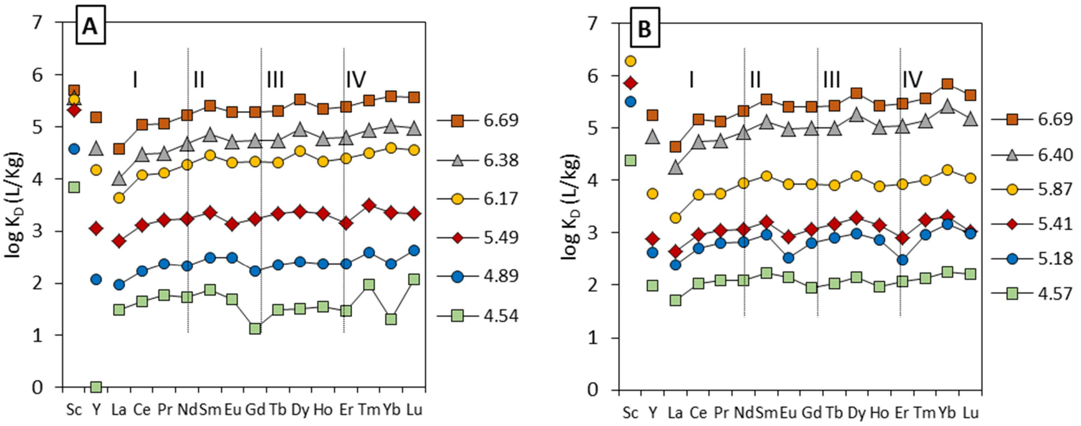

Fig. 2. Log K_D values at different pH values showing the lanthanide M-type tetrad effect: (A) solutions with 20 mM SO_4; (B) solutions with 2 mM SO_4.

Bau (1999) observed an important positive Ce anomaly in hydrous ferric oxide precipitated with REE in the absence of sulfate that was attributed to the oxidation of Ce and the precipitation of CeO_2. This anomaly was not observed in the present experiments (Fig. 2), nor was it observed by Verplanck et al. (2004) in the precipitates obtained after neutralizing acid mine waters with high sulfate concentrations. This observation suggests that sulfate may inhibit Ce oxidation due to sulfate complexation.

According to its ionic radius, Y is commonly displayed between Dy and Ho, where it presents a negative anomaly (not shown in Fig. 2), as evidenced by the K_D^Y/K_D^{Dy} and K_D^Y/K_D^{Ho} ratios below unity (Table S6). The Y anomalies in amorphous Fe(III)-hydroxides were attributed to covalent interactions with the Fe solids (Quinn et al., 2004). The negative Gd and Yb anomalies at lower pH values in the experimental set with 20 mM SO_4 were not previously reported in the literature for similar experiments (Bau 1999; Quinn et al., 2006a,b) and are attributed to analytical errors.

3.3 REE distribution in the column experiment

The complete set of pore water analyses can be found in Table S7 and a selection is plotted in Fig. 3. Only Sc, La and Y were compared due to their different sorption-pH behavior. Both, La and Y were representative of the LREE and HREE, respectively, and their measured values were always above the detection limits.

Essentially, for a given time the pH increased with depth, and for a given depth the column was progressively invaded by more acidic water (Fig. 3A). For each time, Fe and Al concentrations decreased with depth to detection level suggesting the precipitation of schwertmannite and basaluminite (Fig. 3B-C). However, Al showed a peak of concentration higher than the input AMD. This was already observed in previous column experiments, and attributed to the re-dissolution of basaluminite by the percolating AMD once the calcite reagent was exhausted (Rötting et al., 2008a). Practically no Al and Fe were detected at the end of the column in the four sampling events.

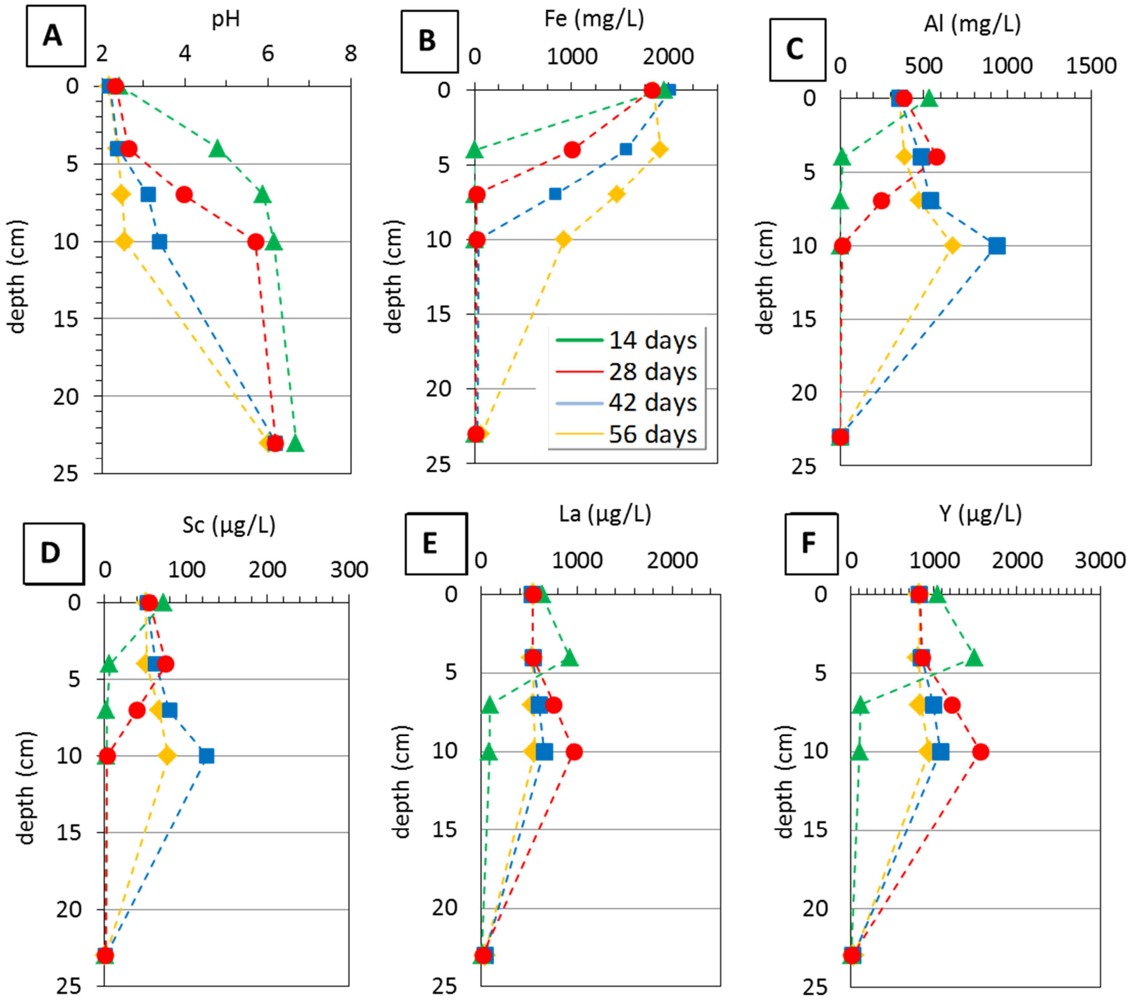

Fig. 3. Depth profiles of pore water and solid composition at four different stages of column operation: (A) pH evolution; (B, C) Fe and Al concentrations in pore water; (D, E, F) mineral distributions; (G, H, I) concentrations of selected REE in pore water.

The concentration of the three selected REE showed a similar distribution pattern (Fig. 3D-F). As described for Al, the concentration decreased with depth, also showing a peak of concentration higher than the input AMD. This distribution suggests a close association of REE to basaluminite, as already observed for Y and lanthanides in previous experiments (Ayora et al., 2016). In subsequent samplings, the peak concentration decreased to the value of the inflow AMD value. Scandium, however, showed a slightly different behavior. For the same sampling event (28 days), the Sc peak was observed to occur upstream with respect to those of La and Y, and for the same depth (10 cm), the Sc peak took longer time to disappear. As for Fe and Al, almost no REE concentration was detected at the end of the column during the experiment.

After a few weeks of functioning, the column showed a distinct zonation with depth (Fig. 4A). The experiment was stopped and the column dismantled after 58 days of functioning. The solid residue was drained, dried and sliced for analysis. The complete set of sequential extraction analyses can be found in Table S8, and a selection is plotted in Fig. 4B-E.The presence of schwertmannite in the samples from the uppermost half of the column was indicated by the amount of Fe recovered in steps II and III of the sequential extraction (Fig. 4B). The presence of schwertmannite and minor goethite together with gypsum and residual calcite (data not presented) was confirmed by XRD. Although not identified on XRD due to its amorphous nature, the presence of basaluminite was evidenced by the amount of Al recovered in the second and third steps of the sequential extraction of samples of the lowermost half of the column (Fig. 4C). The presence of gypsum throughout the column was confirmed by the amount of Ca and S leached in extraction step I and the presence of calcite by the high amount of Ca present in extraction step II (data not presented). This solid phase distribution along the column is identical to that observed in other column experiments and field scale treatments (Rötting et al., 2008a,b; Caraballo et al., 2009, 2011).

As evidenced in Fig. 4D-E, a minor proportion of Sc and the rest of the REE was found in the water-soluble step I, most likely linked to gypsum (Lin et al., 2019). However, most REE were found in steps II and III, which are representative of schwertmannite and basaluminite. However, some differences are evident in the depth distribution of Sc and the rest of the REE. Yttrium (and lanthanides) match the Al distribution along the column depth (Fig. 4E), indicating that they are attached to basaluminite. However, up to 25% Sc was located in the first 6 cm of the column, matching the Fe distribution and suggesting a link to schwertmannite.

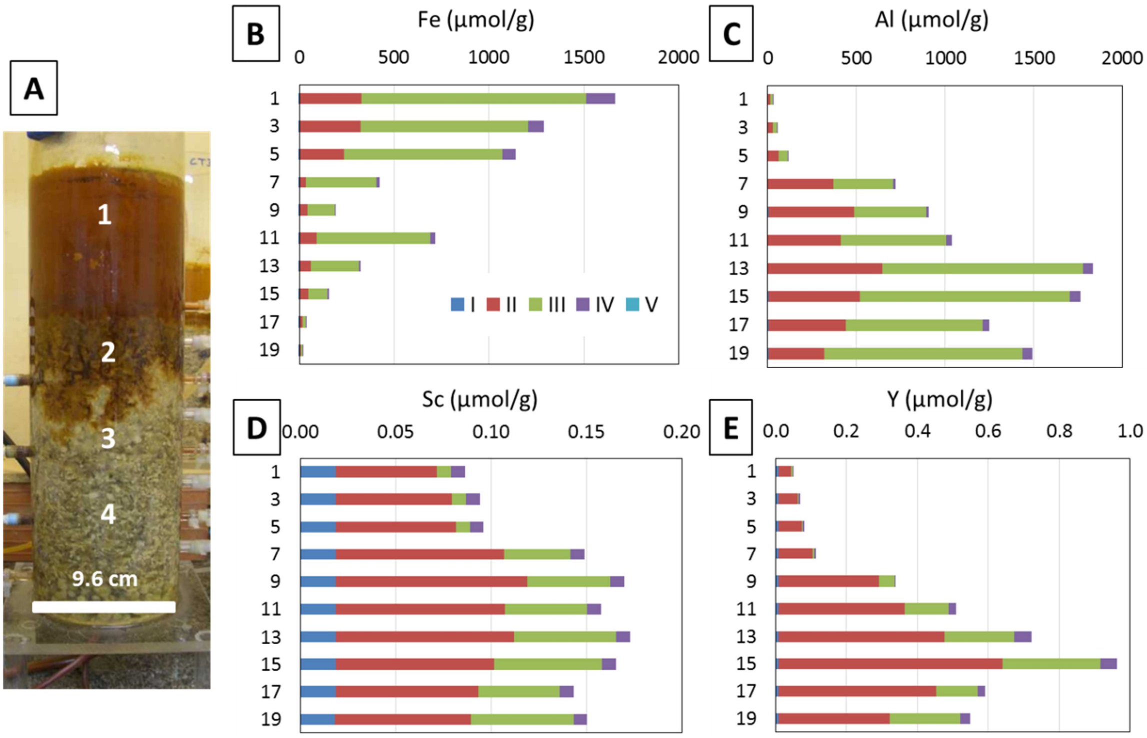

Fig. 4. A) View of the column after 28 days of the experiment: 1= supernatant AMD; 2= schwertmannite zone; 3= basaluminite zone 4= calcite zone. B-E) Distribution of Fe, Al, Sc and Y concentration in the solid residue. The numbers on the vertical axes indicate the depth (cm) of the center of each slice of the column. The colors indicate the different steps of sequential extraction of the following phases: I) the water-soluble fraction; II) calcite and basaluminite, III) low crystalline Fe(III)-oxyhydroxides and remaining basaluminite, IV) crystalline Fe(III)-oxides, and V) the residual fraction.

4 Discussion

4.1 Model description and validation

Different surface complexation models have been commonly used to reproduce experimental REE sorption onto amorphous ferric hydroxide, hematite and goethite. Traditionally, REE sorption onto ferric, manganese and/or aluminum hydroxides/oxides has been explained by the process of free ion sorption onto mineral surface sites. Some models consider the electrostatic term, which accounts for the effect of surface charge on the sorption of free ions or hydrolysis products (Tochiyama et al., 1996; Rabung et al., 1998; Marmier et al., 1997; Marmier and Fromage, 1999; Quinn et al., 2006a). In contrast, a non-electrostatic model can be used when the chemical interaction of the adsorbed cations is stronger than the electrostatic forces present during sorption (Davis and Kent, 1990) and the electrostatic term can be omitted. Here, a non-electrostatic model is proposed to describe the REE sorption based on the practical identity of the titration curves of schwertmannite suspensions under different ionic strengths (Fig. S5). Similarly, some previous studies have proposed a non-electrostatic model to predict REE adsorption on basaltic rock (Tertre et al., 2008) and the sorption of Y and the lanthanides onto amorphous iron hydroxides (Rabung et al., 2000; Quinn et al., 2006a,b) and onto basaluminite (Lozano et al., 2019).

Instead of developing a surface complexation model with free metal ions, sorption of aqueous sulfate complex MSO_4^+ is proposed because sulfate complexes are predominant in AMD waters and in the synthetic solutions prepared for the experiments (Fig. 5A,C). In contrast, REE-carbonate aqueous species were not considered because the proportion of carbonate species is very low at the pH range and sulfate concentrations used in the experiments.

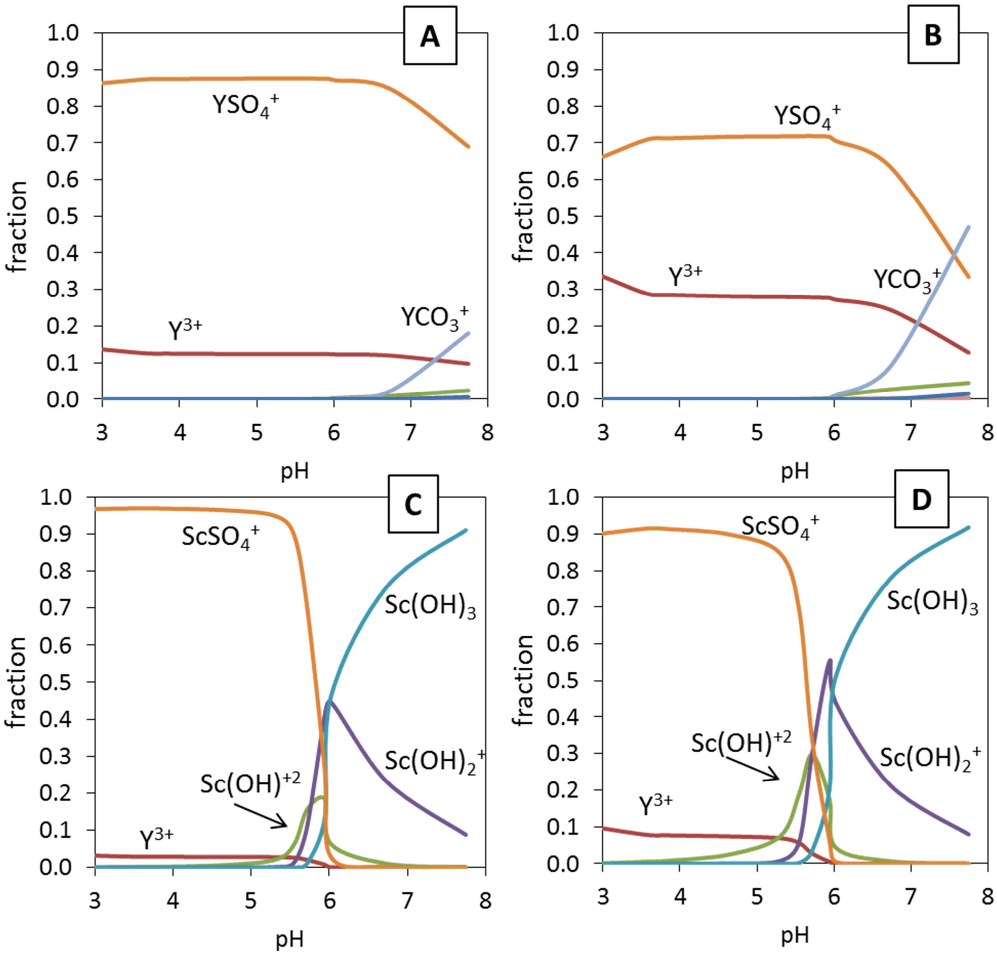

Fig. 5. Aqueous species distribution of Y and Sc (0.01 mM) with different pH values in solutions of 20 mM (A, C) or 2 mM (B, D) sulfate at 25°C and atmospheric CO_2 pressure.

The sorption reaction consists of the exchange of the M^{z+} aqueous complex, (M^{z+} accounting for MSO_4^+ or $Sc(OH)_2^+$) with n protons from the n surface sites (XOH), reflecting the pH dependence mentioned in section 3.2:

$$M^{z+} + nXOH = (XO)_n M^{z-n} + nH^+ \qquad K_M \tag{3}$$

The equilibrium constant, K_M, of the surface complexation reaction for each REE aqueous complex (M) would be:

$$K_M = \frac{[(XO)_n M^{z-n}] \cdot a_{H^+}^n}{a_{M_4^{z+}} \cdot [XOH]^n} \tag{4}$$

where $[(\mathrm{XO})_\mathrm{n}\mathrm{M}^{\mathrm{z-n}}]$ and [XOH] account for the mole fraction of the sorbed species ($[(\mathrm{XO})_\mathrm{n}\mathrm{M}^{\mathrm{z-n}}]/[\mathrm{T}_{\mathrm{XOH}}]$, and of the free surface sites ($[\mathrm{XOH}]/\mathrm{T}_{\mathrm{XOH}}$); and $\mathrm{a}_{\mathrm{M}_4^{\mathrm{z+}}}$ and $\mathrm{a}_{\mathrm{H+}}^{\mathrm{n}}$ represents the activities of the aqueous complex and proton, respectively. Considering aqueous speciation previously described, the total dissolved REE is assumed to be MSO_4^+. A total surface site concentration T_{XOH} of 1.367 mmol/L was assumed according to the schwertmannite surface properties described in section 3.1. The equilibrium constants expressed in this work are equivalent to those referred to as the K_3 in the model 3 proposed by Wang and Giammar (2013), where the surface mole fraction is proposed to better described the mass action expression for bidentate sorption. The concentration of free surface sites was calculated as the difference between the total surface site concentration and the total of REE sorbed:

$$[\mathrm{XOH}] = \mathrm{T}_{\mathrm{XOH}} - \sum \mathrm{n}\,[(\mathrm{XO})_\mathrm{n}\mathrm{M}^{\mathrm{z-n}}] \tag{5}$$

Data from the experiment with 20 m SO_4 was used to calculate the equilibrium constant. Thus, Eq. 4 was rearranged after taking logarithms obtaining a linear expression showed in Eq. 6:

$$\log\frac{[(\mathrm{XO})_\mathrm{n}\mathrm{M}^{\mathrm{z-n}}]}{\mathrm{a}_{\mathrm{M}^{\mathrm{z+}}}} - \mathrm{n}\log[\mathrm{XOH}] + (\mathrm{n}-1)\log\mathrm{T}_{\mathrm{XOH}} = \mathrm{n\,pH} + \log\mathrm{K}_\mathrm{M} \tag{6}$$

The amount of occupied sites with sorbed REE was lower than 10% at high pH experiments, and decreases for lower pH values. Therefore, the concentration of free sites [XOH] can be approximated to that of total sites T_{XOH}, and equation 6 can be simplified:

$$\log\frac{[(\mathrm{XO})_\mathrm{n}\mathrm{M}^{\mathrm{z-n}}]}{\mathrm{a}_{\mathrm{M}^{\mathrm{z+}}}} - \log\mathrm{T}_{\mathrm{XOH}} = \mathrm{n\,pH} + \log\mathrm{K}_\mathrm{M} \tag{7}$$

The experimental data was plotted according to Eq. (7) where the slope with respect to the pH indicated the denticity of the surface complex and the equilibrium constant was obtained from the intercept. The slope varies from 1.4 to 2, increasing with ionic radius, but in general the values are close to 2 (Fig. S6), indicating the tendency to form bidentate surface complexes. Therefore, bidentate surface complexes were assumed for simplification, although a proportion of monodentate complexes could also be present. The equilibrium constants were obtained as the intercept of a straight line of slope 2 by fitting the experimental data set of 20 mM SO_4, according to equation (7). Gnuplot v. 5.7.2 software (Williams and Kelley, 2019) was used for the regression fitting. The error of the regression was larger and included the analytical error, and, therefore, it was assumed to be the error of log K_M value.

Scandium aqueous speciation showed that in addition to $ScSO_4^+$, $Sc(OH)^{2+}$ and $Sc(OH)_2^+$ species are also relevant in the pH range studied (Fig. 5C,D). The linear regression of Eq. (7) for $ScSO_4^+$ experimental data in sorption with high sulfate concentration showed a slope close to 2 (Fig. S7). Although $Sc(OH)_2^+$ species becomes relevant from pH 5, the correlation with pH was very poor and it was not considered. In contrast, Sc $(OH)^{2+}$ showed a good linear regression which resulted in a slope of 1.49 (Fig. S7). Thus, similar to Y and lanthanides, $ScSO_4^+$ and Sc $(OH)^{2+}$ are assumed to form bidentate surface complexes. Similar bidentate complexes were obtained by EXAFS fitting analysis of Lu sorbed onto ferrihydrite and Eu sorbed onto hematite (Dardenne et al., 2001; Estes et al., 2013). On the contrary, REE are found to form monodentate surface complexes in basaluminite (Lozano et al., 2019). Also, Rabung et al. (2006) obtained that Lu formed monodentate surface complexes on γ-Al_2O_3 after fitting EXAFS spectra. This is probably because the Fe-O bond is longer than Al-O, and it provides more space to allocate bidentate surface complexes.

The calculated log K_M values with the errors for the bidentate surface complexation reactions are displayed in Table 1. Equilibrium constants increased from -7.96 to -7.13 from La to Lu, indicating the higher affinity of HREE than LREE for schwertmannite surface.

Element	Surface complex	Log K^2_M	Error
Sc	$(XO)_2ScSO_4^-$	-5.27	0.08
	$(XO)_2ScOH$	-3.4	0.11
Y	$(XO)_2YSO4^-$	-7.62	0.04
La	$(XO)_2LaSO4^-$	-7.96	0.15
Ce	$(XO)_2CeSO4^-$	-7.60	0.10
Pr	$(XO)_2PrSO4^-$	-7.52	0.13
Nd	$(XO)_2NdSO4^-$	-7.44	0.09
Sm	$(XO)_2SmSO4^-$	-7.27	0.08
Eu	$(XO)_2EuSO4^-$	-7.41	0.09
Gd	$(XO)_2GdSO4^-$	-7.51	0.05
Tb	$(XO)_2TbSO4^-$	-7.42	0.06
Dy	$(XO)_2DySO4^-$	-7.27	0.03
Ho	$(XO)_2HoSO4^-$	-7.38	0.06
Er	$(XO)_2ErSO4^-$	-7.39	0.05
Tm	$(XO)_2TmSO4^-$	-7.17	0.08
Yb	$(XO)_2YbSO4^-$	-7.26	0.04
Lu	$(XO)_2LuSO4^-$	-7.13	0.09

Table 1. REE surface complexation constants for bidentate surface complexes obtained by fitting the experimental equation 7 with a concentration of 20 mM SO_4 and a surface site d concentration of 1.367 mmol/L.

The sorption edge for each REE was calculated with the PHREEQC software. As expected, the calculations match the experimental data set of 20 mM SO_4 (Fig. 6). The predicted and experimental sorption edges for the complete set of REE are shown in Fig. S8. With the exception of a slight overestimation for La, the model fit the concentration of the rest of the lanthanides and Y within the experimental error (Fig. S8). Regarding Sc, the good fit observed between the model-predicted outcome and the measured from experiments confirmed the existence of two different surface species. This result highlights the different behavior of Sc sorption with respect to the rest of the REE and is a consequence of its different aqueous speciation. On the atomic scale, the Sc ionic radius is 0.75 Å (Rudolph and Pye, 2000), which is considerably lower than that of Lu, the smallest radius of the lanthanide series (0.98 Å).

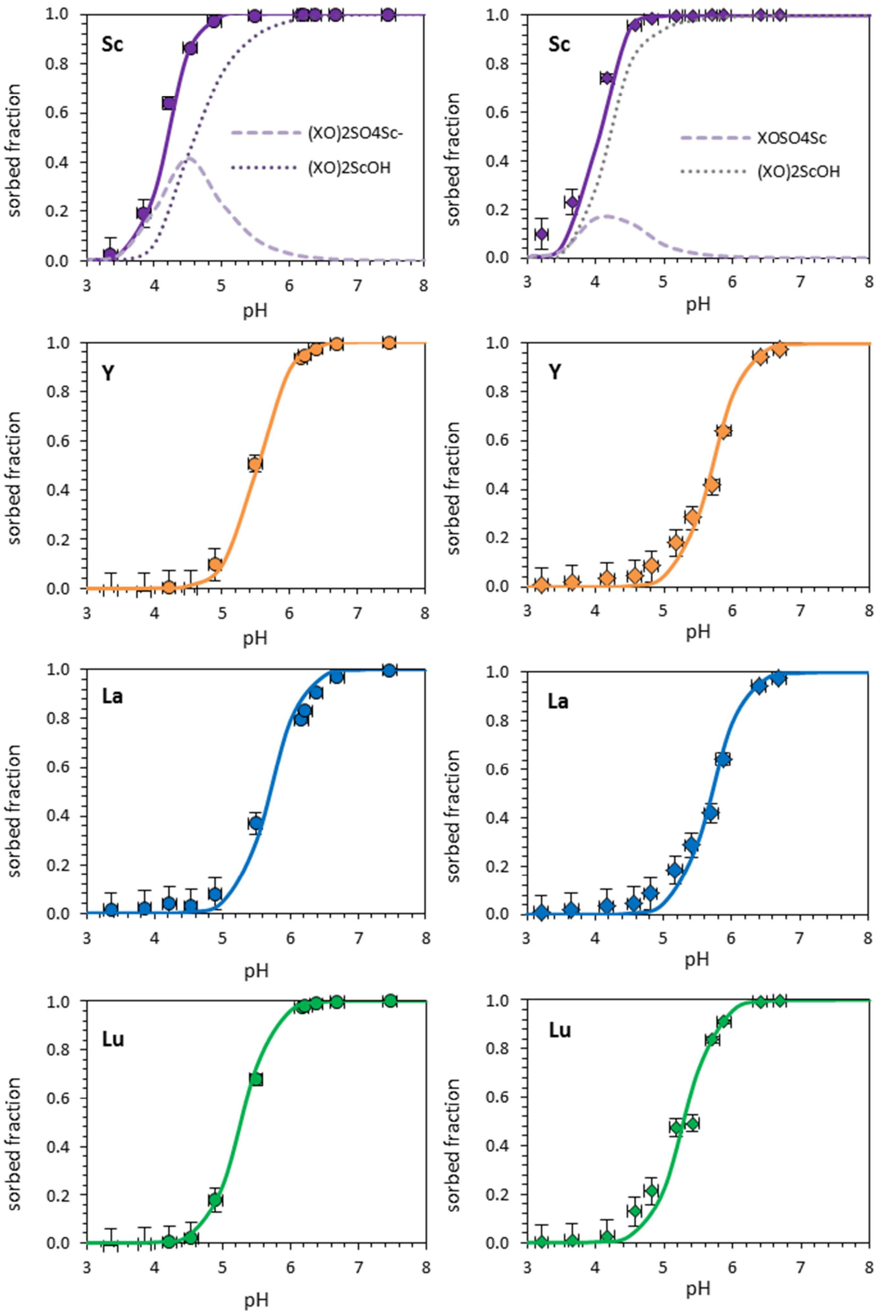

Fig. 6. Experimental (symbols) and calculated fractions (lines) of the sorption curves for Sc, Y, La and Lu for the experiments with 20 mM SO_4 (left column) and with 2 mM SO_4 (right column). Calculations at 25°C and atmospheric CO_2 pressure.

The model constructed with the 20 mM SO_4 experimental data set was validated with three additional data sets: one set with 2 mM SO_4 and a solid:liquid ratio of 1 g/L, and another two sets with 20 mM SO_4 and solid:liquid ratios of 0.25 g/L and 2 g/L, respectively. The experimental and predicted values for Y, La, Lu and Sc for 2 mM SO_4 and 1 g/L solid:liquid ratio are plotted in Fig. 6 (right column). The predicted and experimental values for the complete set of REE are shown in Fig. S9. Although with a slight underestimation at lower pH values, the modeled curves match the experimental sorption at lower sulfate concentrations within the experimental error, confirming the formation of bidentate surface complexes.

The comparisons between the modeled and experimental data of selected elements for 1, 2 and 0.25 g/L solid:liquid ratios are shown in Fig. 7, and the data for the complete set of REE are plotted in Fig. S10. Despite a slight overprediction at higher pH values for the 0.25 g/L solid:liquid ratio, the sorbed fractions for the different suspension concentrations were successfully predicted by the model within the experimental errors.

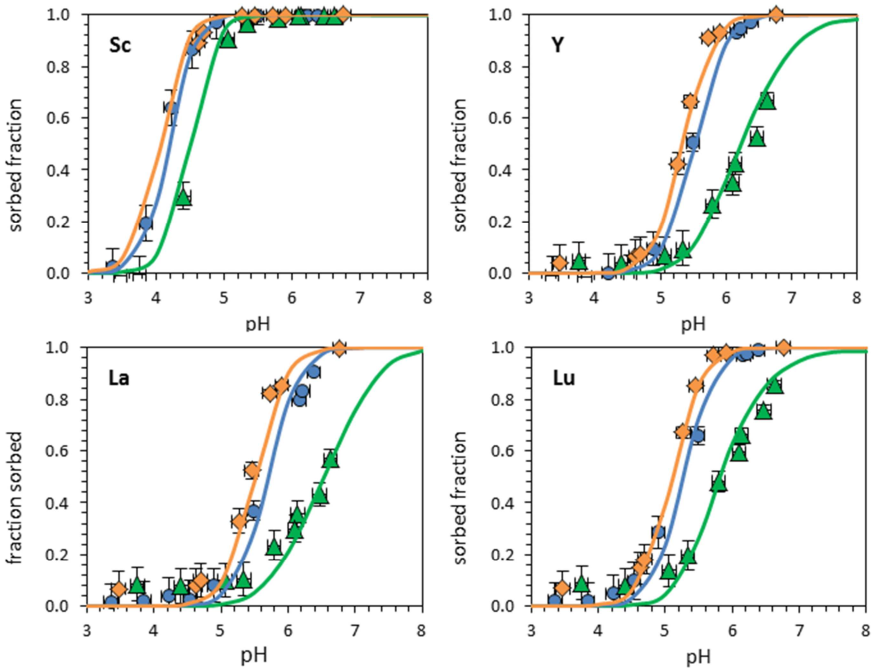

Fig. 7. Experimental data (symbols) and predicted sorbed fraction (lines) for sorption in 20 mM SO_4 in solution and solid:liquid ratios of 2 g/L (orange diamonds), 1 g/L (blue circles) and 0.25 g/L (green triangles). Calculations at 25°C and atmospheric CO_2 pressure.

4.2 REE mobility in an AMD neutralization column

The results of the 1D reactive transport model will be used to interpret the experimental data of Fig. 3 and Fig. 4. The results of the calculations for aqueous pH and for major solutes in pore water and the amount of mineral dissolved/precipitated are plotted in Fig. 8A-F. For a given time the pH increased with depth, and for a given depth the column was progressively invaded by more acidic water. A schwertmannite front appeared first, at lower pH values (pH 2.5), followed by a basaluminite front (pH 3.8), and both fronts advanced with time (Fig. 8D,E). The calculations confirm that when calcite started to be exhausted from the top of the column downwards (Fig. 8F), the acid water, although did not affect to the precipitated schwertmannite, it dissolved the basaluminite and the Al concentration in the pore water increased above the inflow concentration (Fig.8C).

According to Fig. 6 and 7, Sc sorbs from pH 3, so this element could also sorb on schwertmannite precipitates. Unlikely, lanthanides and Y start to sorb at least one pH unit higher and sorption of these elements was only expected in basaluminite. These differences are reflected in the log K values, which were similar between La and Y but clearly differed with respect to Sc values. Thus, the similar La and Y distribution in pore water in contrast to the different behavior of Sc with respect to La and Y was evidenced in both the measured and calculated pore water concentrations (Fig. 8 G-I).

For each time span, the different mobility between Sc, Y and lanthanides due to sorption processes depends on the pH at a given depth, which is in turn related to the schwertmannite and basaluminite precipitation. Thus, after two weeks, at 4 cm deep, the pH was 4.8, and Sc was completely sorbed, whereas La and Y, which had previously sorbed at an earlier time, were partially desorbing (notice their higher concentrations in the pore water than in the inflow). At 7 cm and deeper points, the pH was close to 6, and again, the three REE were sorbed. After four weeks and at 4 cm deep, the pH was 2.6, and Sc was desorbing, whereas La and Y were already desorbed (their concentrations were already equal to the inflow). At 7 cm deep, the pH was 4.1, and Sc was partially sorbed, as demonstrated by its concentration being lower than that in the inflow, and La and Y were desorbing, as shown again by their higher concentrations than those in the inflow. At 10 cm deep and with a pH of 5.7, Sc was entirely sorbed, whereas La and Y were already partially desorbing. After six weeks and at 4 cm deep, the pH remained at 2.5, and all three REE were completely desorbed. Meanwhile, at 7 and 10 cm deep with a pH of 3.1 and 3.4, respectively, Sc was still desorbing, whereas La and Y were practically desorbed. After 8 weeks, all three REE were desorbed at all recorded depths, with the exception of Sc, which was partially desorbed. At the end of the column (23 cm deep), the concentration of REE was very low throughout the experiment.

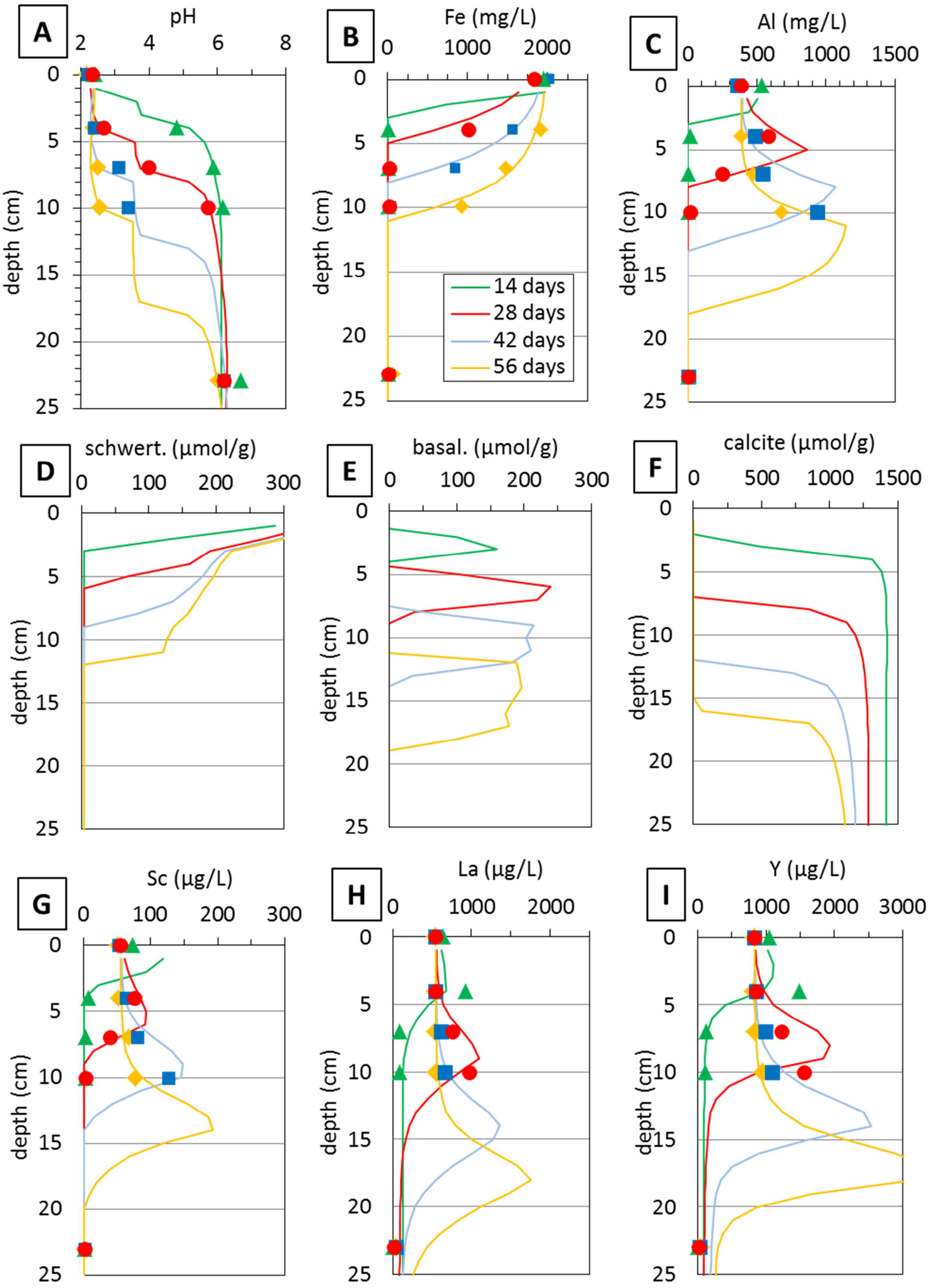

Fig. 8. Depth profiles of experimental data (symbols) and the reactive transport model (lines) at four different stages of column operation: (A) pH evolution; (B, C) Fe and Al concentrations in pore water; (D, E, F) mineral distributions; (G, H, I) concentrations of selected REE in pore water.

The calculated solid phase distribution at the end of the column life (Fig. 8D-E, 56 days) was also consistent with that deduced from sequential extraction analyses (Fig. 4B-C). Thus schwertmannite was predicted to form between 0 and 11 cm, especially in the shallower 4 cm. A basaluminite zone was calculated to develop between 11 and 20 cm, comparable to the observed range between 7 and 20 cm. The calculated pH value in the lowermost 10 cm ranged from 3.8 to 6, indicating that La, Y and Sc could remain sorbed on basaluminite, in accordance with sequential extraction analyses and with the absence of REE in the column outflow. However, the presence of some REE, and particularly Sc (up to 25%) in the uppermost 10 cm of column deserves further discussion. The calculated pH value in the uppermost 10 cm was 2.5, buffered by schwertmannite precipitation. At such pH, basaluminite was dissolved releasing to the pore water all the REE sorbed in earlier stages of the column. Also Sc, if partially sorbed on schwertmannite would be desorbed (Fig. 7, high solid:liquid ratio). Therefore, the Sc analyzed in the upper 10 cm of solid residue indicates that desorption was not entirely reversible. Indeed, desorption has also been reported to be a very slow process in experiments of Yb sorption on hematite and alumina (Marmier et al., 1997).

5 Conclusions

The experimental results confirm that the sorption of REE onto schwertmannite is highly dependent on pH. For a solid:liquid ratio of 1 g/L, the sorption of the lanthanide series and Y is significant from pH 5, and the REE were almost totally sorbed at pH 6.5, depending on the element. The sorption of Y and lanthanides were not affected by the amount of sulfate in solution, probably because MSO_4^+ is the overwhelming aqueous species above 1 mM SO_4, but Sc slightly increased with lower sulfate content because in addition to $ScSO_4^+$, the $ScOH^{2+}$ aqueous species was also sorbed, showing an important Sc sorption fraction at pH values at which the sorption of rest of REE is almost negligible. This suggests that, in active treatment plants, Sc can be segregated from the rest of REE by keeping the pH of the process below 4.5.

The results of the sorption experiments were explained by a non-electrostatic model in which MSO_4^+ (and $ScOH^{2+}$) exchanges with two surface protons, forming a bidentate surface complex. Similar to other iron and aluminum oxides/hydroxides, preferential sorption was observed from La to Lu with an important enrichment also in Sc. Thus, sorption mechanism controls the mobility of which can be totally removed at circumneutral pH values. Moreover, due to the enrichment in HREE and Sc, REE- rich schwertmannite precipitates can become in a profitable resource.

The sorption model was applied to predict the REE behavior in a laboratory column simulating a passive AMD remediation system. As AMD infiltrates the column, calcite dissolves, the pH increases and schwertmannite precipitates. The progression of neutralization raises the pH above 4, and basaluminite forms. As a result, two fronts form: basaluminite progressing at a higher pH on the limestone column and schwertmannite behind, progressing at lower pH values. The model successfully predicts the analyses of REE in pore water and solid phases. Both the experiments and the model show the behavior of Sc which at lower pH remain preferentially retained in schwertmannite precipitates. Although schwertmannite and basaluminite have similar sorption edges, Y and the lanthanides only sorb at pH values higher than 4.5, and sorption only occurs on basaluminite because schwertmannite forms at pH values lower than 4. In contrast, the Sc sorption edge extends from pH 3 to 5 and therefore can partially sorb on schwertmannite. As a practical consequence, REE preferentially accumulate in the basaluminite residue of AMD passive treatment systems, but a minor significant fraction of Sc can also be found in the schwertmannite waste.

Acknowledgments

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Supplementary material

Sorption of rare earth elements on schwertmannite and their mobility in acid mine drainage treatments

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FIGURE CAPTIONS

Fig. S1. XRD pattern of pure schwertmannite prior to and after the sorption experiments at 20 mM SO_4 and different pH values. Notice that no goethite peaks are observed.

Fig. S2. XRD pattern of pure schwertmannite prior to and after the sorption experiments at 2 mM SO_4 and different final pH values. Notice that no goethite peaks are observed.

Fig. S3. Surface site distribution in schwertmannite. Atoms labeled “A” form the face (1 0 0), “B” form (0 1 0) and “C” form (0 0 1). Data from Fernandez-Martinez et al. (2010).

Fig. S4. Evolution of REE sorbed on schwertmannite (µmol/g) over time at pH 5.5 ±0.2 for selected REEs. (Sc: circles, Lu: diamonds, Y: squares, La: triangles, and dotted line: pH value; Sc*=Sc/2).

Fig. S5. Titration of schwertmannite suspensions (1 g/L) under different $NaNO_3$ concentrations. Symbols: Suspensions with different NH_4OH and HCl addition and kept under stirring for 24 hours. Solid lines: titrations conducted using a 848 Titrino plus titrator with addition of NH_4OH 0.1 M (OH>0) and HCl 0.1 M (OH<0). After each titrant addition, the electrode reading was set between 60 to 120 seconds, and the drift was lower than 50 mV/min. All the experiments were made at 25°C and atmospheric CO_2 pressure.

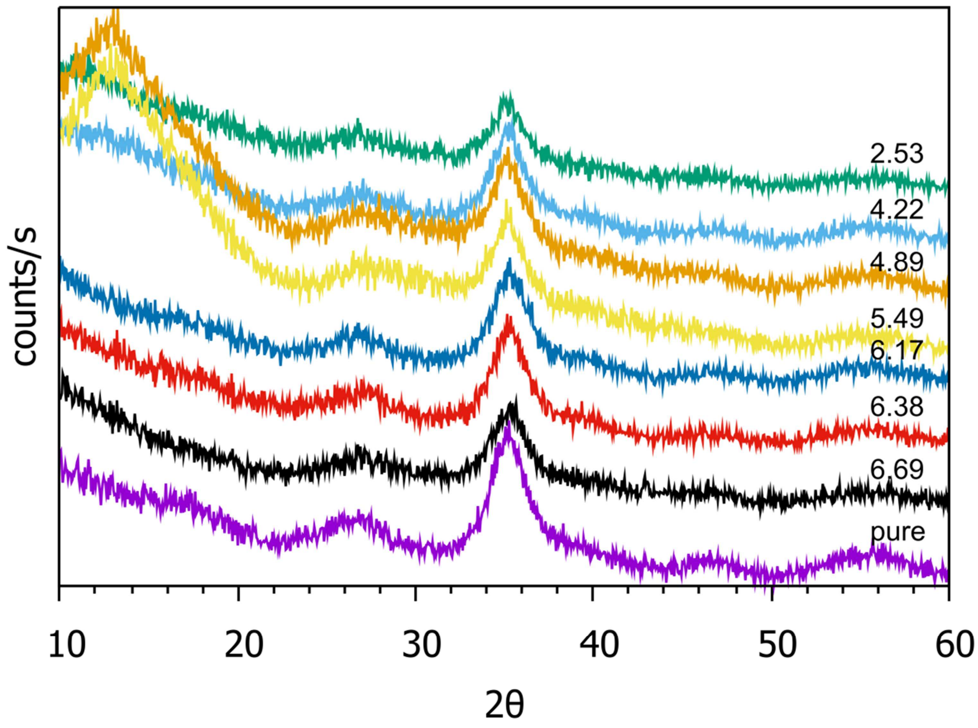
Fig. S6 Regressions obtained from measured pH values and calculated activities from the final concentrations of the experimental data set of 20 mM SO_4. (A, B, C) Regressions for Y, La and Lu, respectively, plotted as Eq. (S5).

Fig. S7 Regressions obtained from experimental data of Sc plotted according to Eq. (S5) for $ScSO_4^+$ (A) and $ScOH^{2+}$ (B) species.

Fig. S8. Sorbed fractions measured (symbols) and calculated (lines) for 20 mM SO_4 and a 1 g/L solid:liquid ratio. Calculations performed at 25°C and pCO_2 of 3.5.

Fig. S9. Sorbed fractions measured (symbols) and calculated (lines) for 2 mM SO_4 and a 1 g/L solid:liquid ratio. Calculations performed at 25°C and pCO_2 of 3.5.

Fig. S10. Sorbed fractions measured (symbols) and calculated (lines) for 20 mM SO_4 and three different solid:liquid ratios: 2 g/L (orange diamonds), 1 g/L (blue circles) and 0.25 g/L (green triangles). Calculations performed at 25°C and pCO_2 of 3.5.



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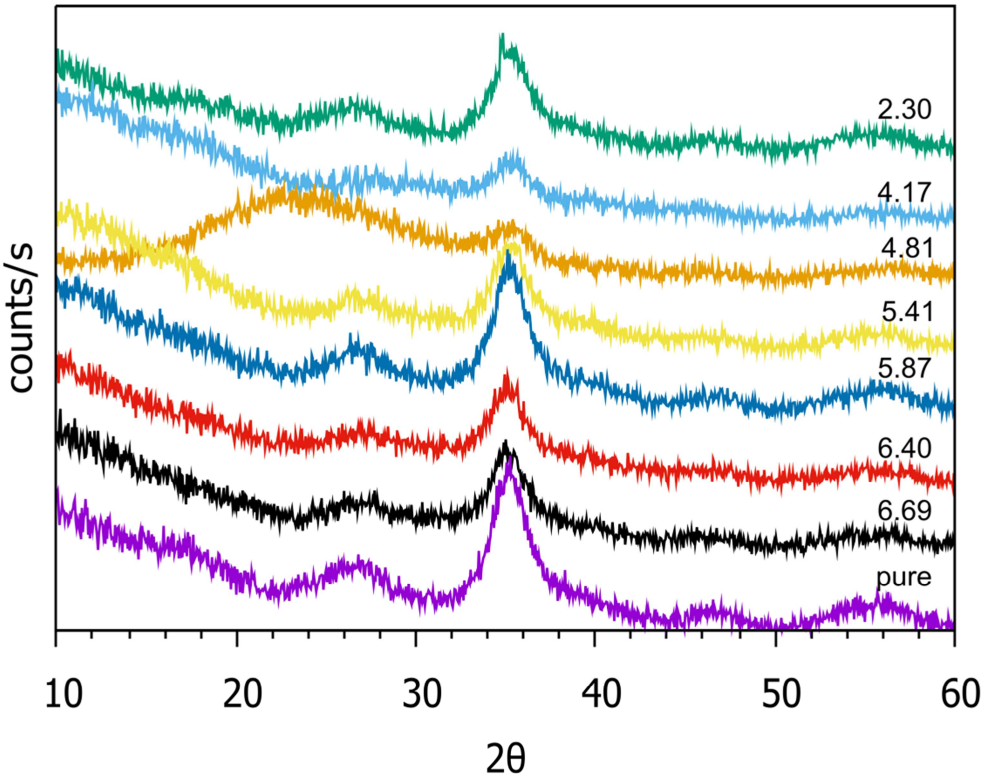
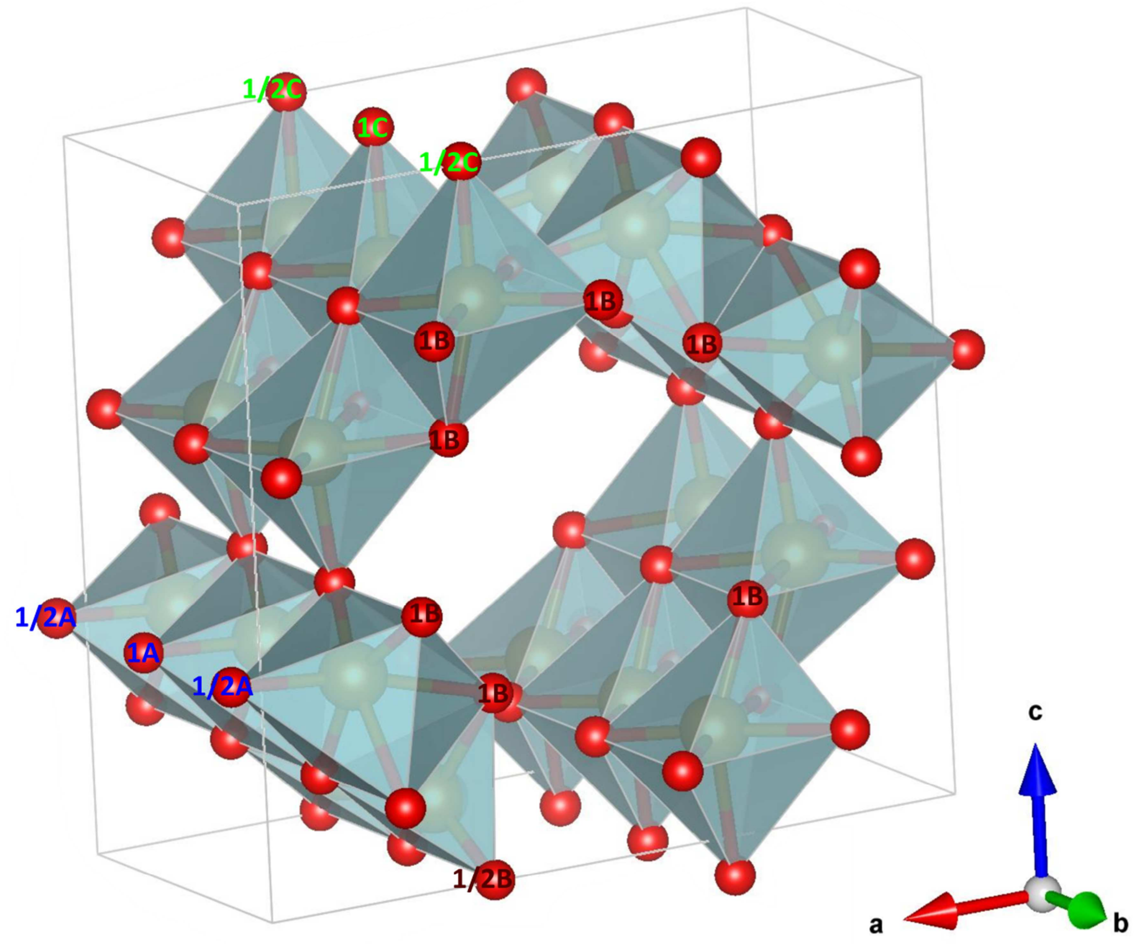


Fig. S2. XRD pattern of pure schwertmannite prior to and after the sorption experiments at 2 mM SO_4 and different final pH values. Notice that no goethite peaks are observed.



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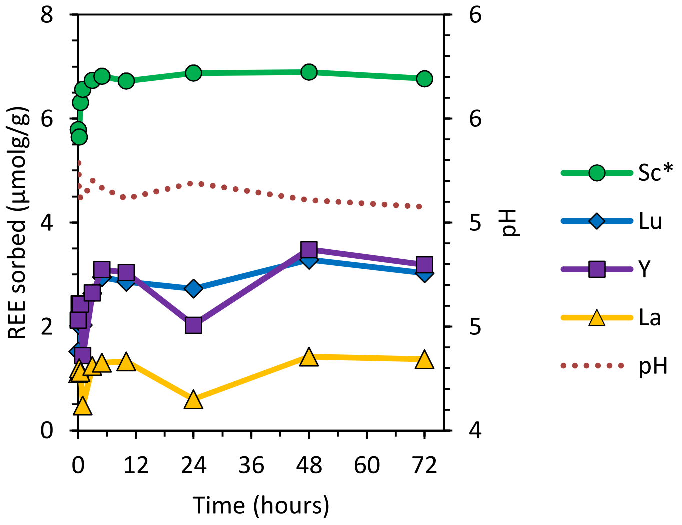

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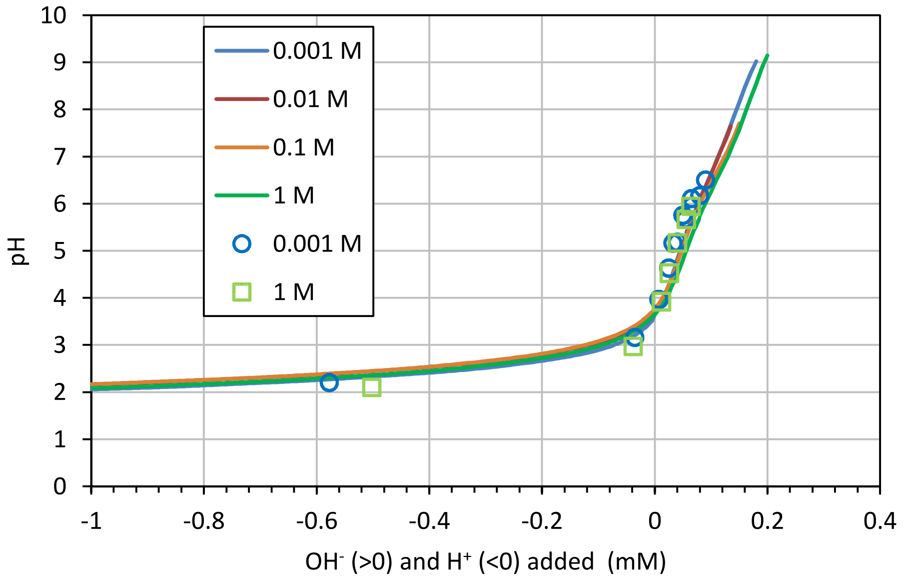

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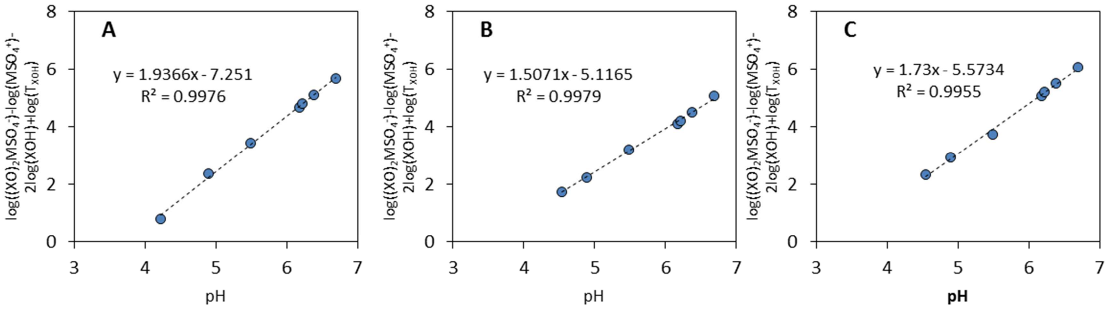

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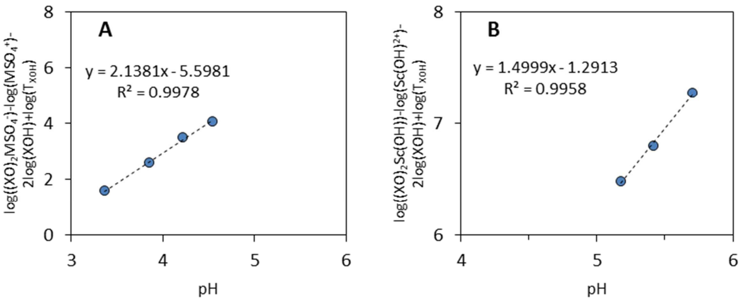

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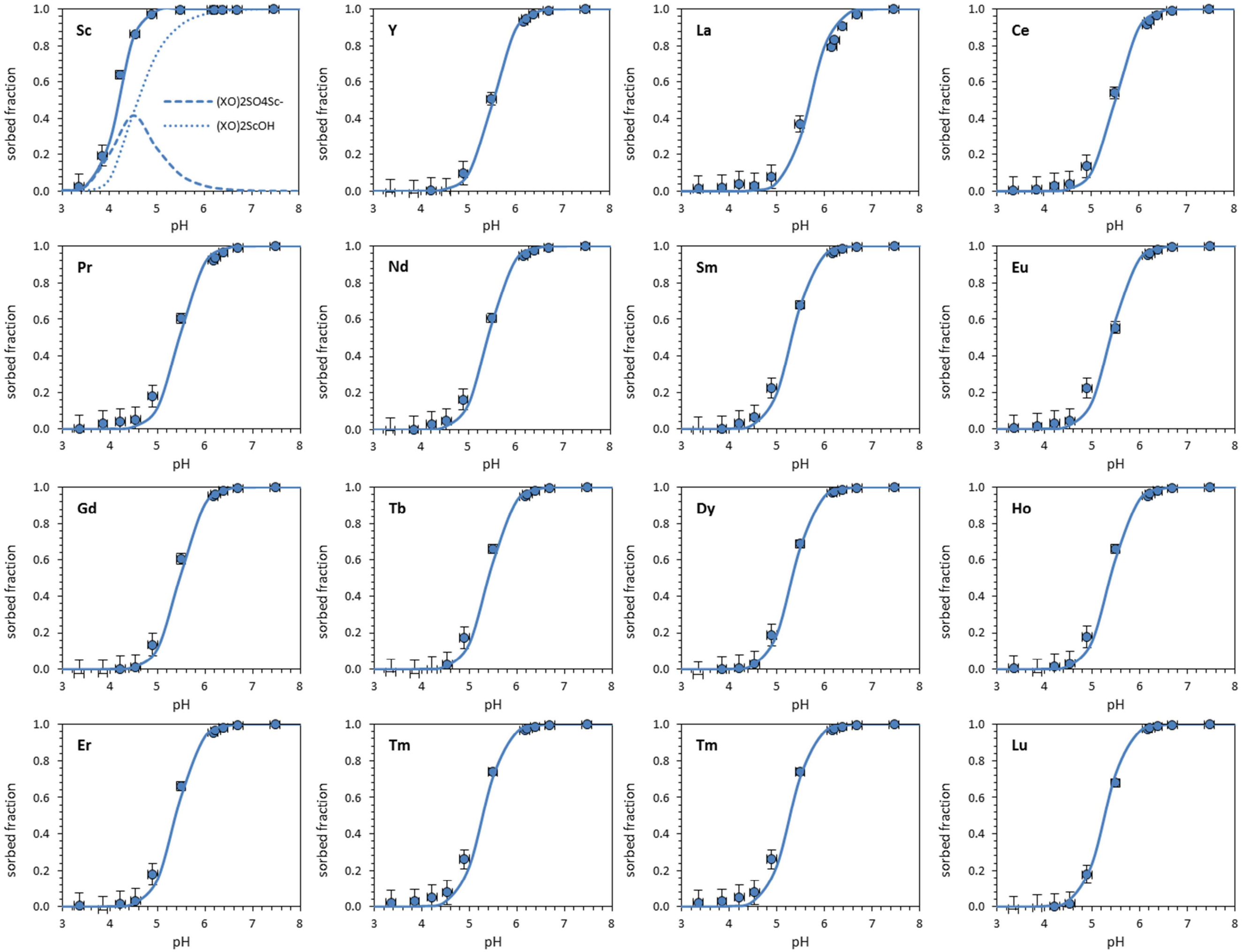

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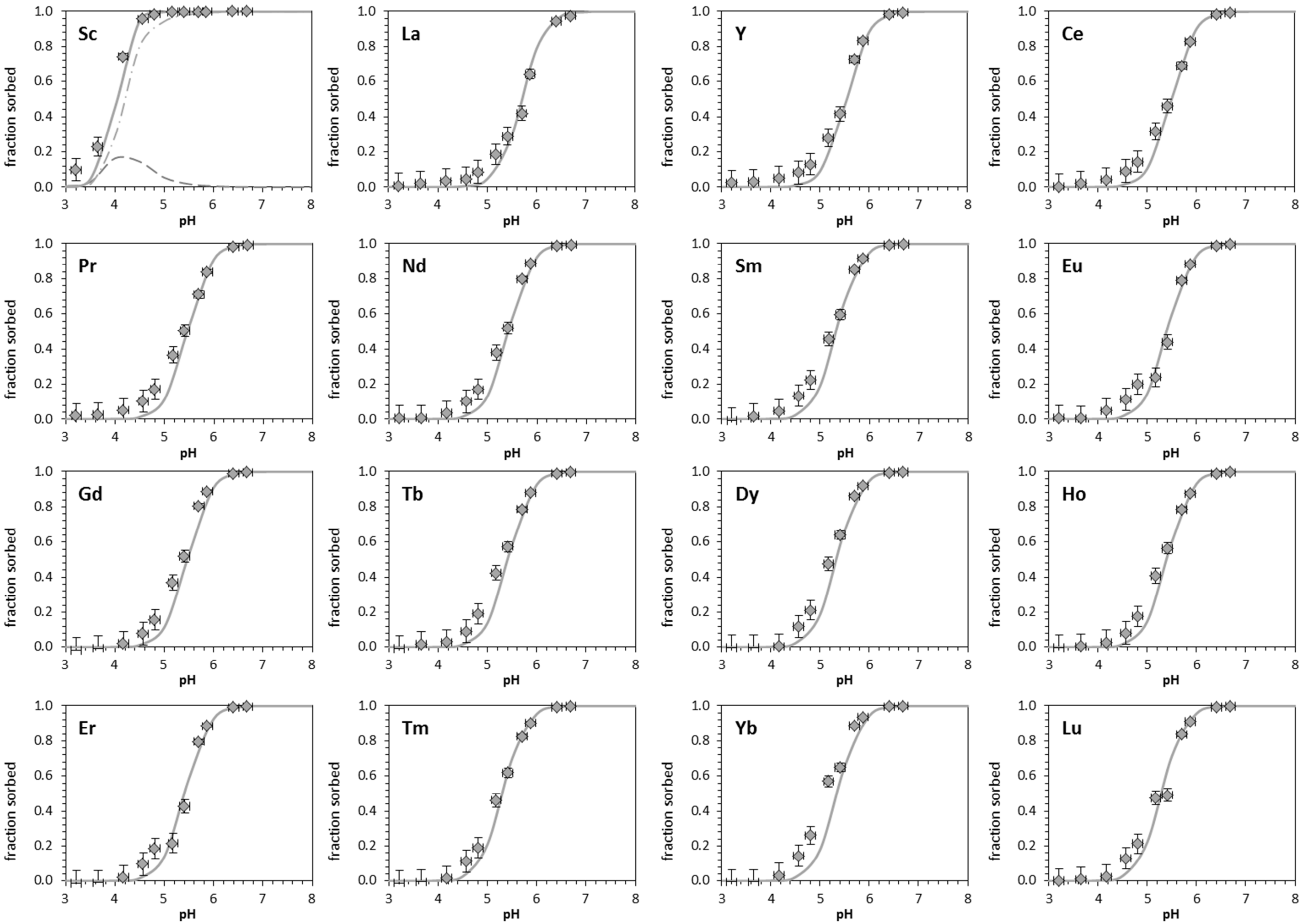

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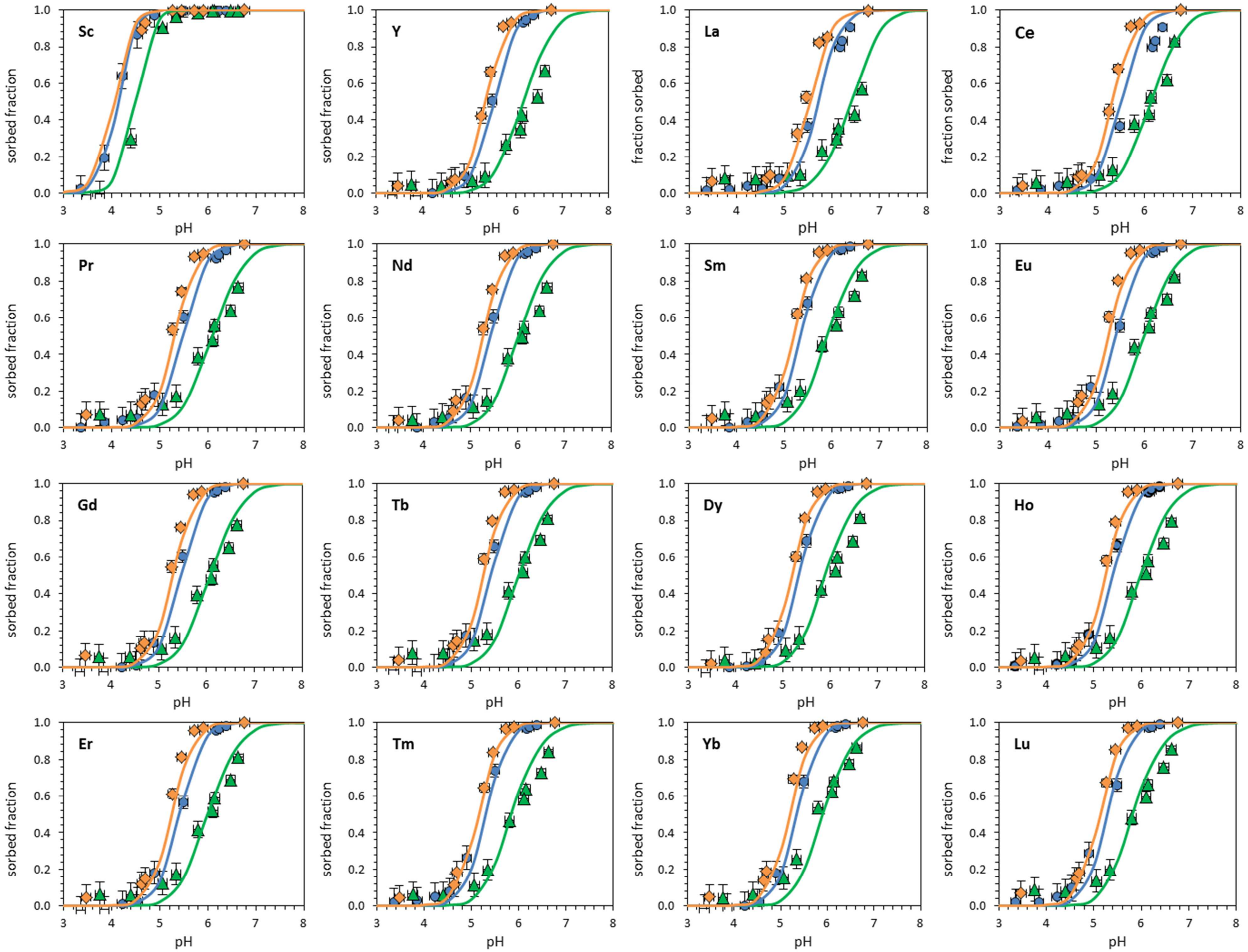

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Article 4

Solid and aqueous speciation of yttrium in passive remediation systems of acid mine drainage.

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Solid and Aqueous Speciation of Yttrium in Passive Remediation Systems of Acid Mine Drainage

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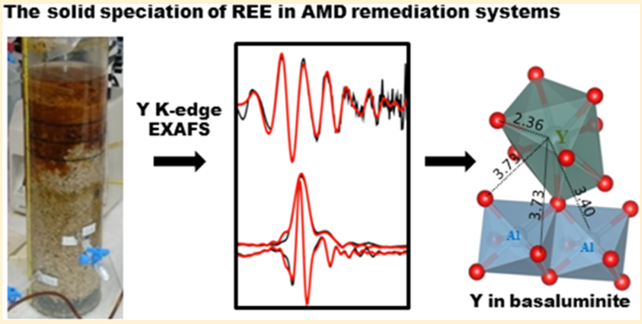
Supporting Information



ABSTRACT: Yttrium belongs to the rare earth elements (REEs) together with lanthanides and scandium. REEs are commonly used in modern technologies, and their limited supply has made it necessary to look for new alternative resources. Acid mine drainage (AMD) is a potential resource since it is moderately enriched in REEs. In fact, in passive remediation systems, which are implemented to minimize the environmental impacts of AMD, REEs are mainly retained in basaluminite, an aluminum hydroxysulfate precipitate. In this study, the solid and liquid speciation and the local structure of yttrium are studied in high-sulfate aqueous solutions, basaluminite standards, and samples from remediation columns using synchrotron-based techniques and molecular modeling. Pair distribution function (PDF) analyses and ab initio molecular dynamics density functional theory models of the yttrium sulfate solution show that the YSO_4^+ ion pair forms a monodentate inner-sphere complex. Extended X-ray absorption fine structure (EXAFS) and PDF analyses show that Y is retained by basaluminite, forming a monodentate inner-sphere surface complex on the aluminum hydroxide surface. EXAFS of the column samples shows that more than 75% of their signal is represented by the signal of basaluminite with which YSO_4^+ forms an inner-sphere complex. The atomic view of the REE configuration in AMD environments could facilitate a deeper research of REE recovery from waste generated in AMD remediation systems.

■ INTRODUCTION

Yttrium belongs to the rare earth element (REE) group, also composed of lanthanides and scandium. REEs are necessary for the development of modern technologies, and specifically, yttrium has important applications, for instance, in fluorescent lamps as phosphors,[1] and in the aircraft industry, used in the thermal barrier coatings for jet engines.[2] The increasing demand for REEs and their low worldwide supply have led to considering REEs as critical raw materials, boosting searches for alternative resources, such as recycling used stocks or identifying new geological sources of these elements. Because the REE concentrations in acid mine drainage (AMD) are from one to two orders of magnitude higher than the average concentrations in natural waters,[3] it may be possible to perform secondary REE recovery from precipitates from AMD neutralization in passive remediation systems. These active systems were developed to minimize the environmental impacts of AMD and they are used worldwide.[4,5] However, due to the high water content, sludge storage has substantial operational costs and environmental concerns.[6,7] In contrast, passive remediation systems, which have been developed extensively in recent decades,[8−11] allow the AMD neutralization generating lower amounts of solid waste precipitates. Ayora et al. documented nearly complete aqueous REE retention in two laboratory columns, simulating a disperse alkaline substrate (DAS), a passive treatment already implemented in the field, for two highly acidic AMDs (SW

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Spain).[12,13] The REEs were scavenged by basaluminite, a mineral precipitated in the columns, which also presented Y enrichment due to the higher yttrium concentration with respect to the rest of REEs in the two treated AMDs. Basaluminite, an aluminum oxyhydroxysulfate ($Al_4(SO_4)(OH)_{10}\cdot 5H_2O$), precipitates in acidic environments as a consequence of the natural attenuation of the AMD when mixed with more alkaline waters, or due to the induced neutralization of the acid waters, when the solution pH reaches ~4.[14] Basaluminite is considered a nanomineral, with a short-range order, around 1 nm of coherent domain size, which is described as layers of Al-octahedra with structural point defects and with sulfate groups as outer-sphere complexes between the Al layers.[15]

Similarly to the REE uptake by basaluminite in DAS treatments, Gammons et al. reported the precipitation of hydrous aluminum oxides accompanied by a decrease in REE concentration from AMD when mixed with natural water.[16] Recently, the scavenging of REEs by basaluminite precipitates has been described as a sorption mechanism.[17] AMD is characterized to contain high loads of dissolved sulfate and the affinity of REEs to form aqueous species with sulfate is very high, the MSO_4^+ aqueous complex being more abundant in AMD solutions.[18] Sorption of dissolved REEs from sulfate-rich waters onto basaluminite is thus described as the sorption of the MSO_4^+ aqueous complex via ligand exchange with a surface site of basaluminite, forming a monodentate surface complex with the Al-octahedron as one proton is released.[17] Here, a structural description of the aqueous YSO_4^+ complex and of the local environment of the surface complex formed upon adsorption onto basaluminite are reported.

Most of the previous studies reporting the adsorption mechanisms of REEs using X-ray absorption spectroscopy and extended X-ray absorption fine structure (EXAFS) described the adsorption of free REE ions onto the surface of metal oxides.[19−22] However, the AMD environments show a high concentration of dissolved sulfate, which presents high affinity for aqueous REEs (M). Thus, the MSO_4^+ aqueous complex is the major REE species in solution, and hence, the sorption models of REEs in AMD precipitates might be better explained in terms of MSO_4^+ sorption.

The structure of the first hydration shell of lanthanides and yttrium has been well characterized.[23−28] The coordination number (CN) of the first hydration shell changes from an average of CN ~ 9 oxygen atoms for light REEs (LREEs La to Pm) to CN ~ 8 oxygen atoms for heavy REEs (HREEs Tb to Lu), with intermediate values for medium REEs (MREEs Pm to Gd).[27] This behavior is explained by the continuous decrease in ionic radii with the atomic number.[27,29,30] The ionic radius of yttrium is between those of Ho and Dy, so it is typically considered an HREE with a first hydration shell of CN ~ 8 oxygen atoms. There are several studies describing aqueous complexes of REEs with different ligands. REEs easily form inner-sphere complexes with carbonate and phosphate in solution,[31−33] whereas chloride and nitrate form inner-sphere complexes at concentrations higher than 10 M.[23,25] In the case of sulfate, no information about the geometry of MSO_4^+ complexes has been reported so far despite their strong binding affinity.[18]

The objective of this study is to elucidate the structure of Y adsorbed onto basaluminite. Its chemical similarities with HREEs allow us to assume similar structural configuration for this subgroup. Moreover, this element was one of the most concentrated in waste samples allowing performing X-ray absorption spectroscopy experiments. Since the YSO_4^+ aqueous complex is adsorbed onto the mineral,[17] a previous characterization of the geometry of the aqueous complex has been carried out. Finally, a quantification of Y-species in basaluminite solids precipitated from AMD treatments has been performed. Structural studies were performed using EXAFS and pair distribution function (PDF) analyses of aqueous and solid samples combined with ab initio molecular dynamics (AIMD) simulations of the aqueous YSO_4^+ complexes.

Two hypotheses are used to investigate the local structure of the aqueous YSO_4^+ ion pair: (1) an outer-sphere complex, with water located between Y^{3+} and SO_4^{2-}, and (2) an inner-sphere complex. In the latter case, two more hypotheses must be considered: (a) a monodentate complex, with one oxygen atom shared between the sulfate and the first coordination sphere of Y^{3+}, and (b) a bidentate complex, with two oxygen atoms shared between the yttrium hydration sphere and the sulfate group.

Once the structure of the aqueous solution is fully described, different hypotheses have been considered to interpret the YSO_4^+ surface complexation onto the Al-oxyhydroxysulfate: the formation of (1) a monodentate inner-sphere complex, (2) a bidentate mononuclear inner-sphere complex, and (3) a bidentate binuclear inner-sphere complex.

Finally, to determine semiquantitatively the yttrium species in solids from column samples, linear combination fits were performed using the most representative references.

■ MATERIALS AND METHODS

Synthetic Samples (Standards). Different basaluminites doped with Y were prepared for high-energy X-ray scattering (HEXS) and EXAFS experiments. To ensure maximum Y incorporation into the solid, sorption and coprecipitation experiments were performed at pH 6,[17] avoiding higher pH values where YCO_3^+ aqueous species could be present.[34] A basaluminite sample with sorbed YSO_4^+ (B-YSO_4-ads) was obtained from a suspension of 1 g/L of solid in 0.11 $Y(NO_3)_3\cdot 6H_2O$ and 0.25 M Na_2SO_4 solution in 5 h at a constant pH of 6. Under these conditions, the major species in solution was YSO_4^+, which is supposedly the aqueous Y species sorbed on the solid surface.[17] A basaluminite sample coprecipitated with Y (B-Ycop) was obtained using the basaluminite synthesis method adding 1 M $Y(NO_3)_3\cdot 6H_2O$ in the acid solution of 0.05 M $Al_2(SO_4)_3\cdot 18H_2O$ (see Chapter S1 of the SI). Basaluminite and nanoboehmite samples with sorbed Y^{3+} (B-Yads and A-Yads, respectively) were also prepared from a suspension of 1 g/L of solid in 0.011−0.11 M $Y(NO_3)_3\cdot 6H_2O$ solution in 5 h, and the pH was maintained at ~6 at room temperature (the synthesis protocol is described in detail in Chapter S1 of the SI). Under these conditions, the major species of Y was Y^{3+}. In all cases, the suspensions were centrifuged at 4500 rpm for 15 min; the supernatant was filtered through 0.2 μm membranes and kept for inductively coupled plasma (ICP) analysis. The solids were rinsed several times with deionized water and oven-dried for 48 h at a maximum temperature of 40 °C.

High-energy X-ray scattering (HEXS) and EXAFS experiments of aqueous solutions with Y and YSO_4^+ were carried out. For the HEXS measurements, an aqueous solution of free yttrium ions (Y-sol) was prepared with 0.1 M $Y(NO_3)_3\cdot 6H_2O$ at pH 3.2, and a solution containing YSO_4^+ as the major aqueous complex (YSO_4-sol) was prepared by mixing equal amounts of 0.2 M $Y(NO_3)_3·6H_2O$ and 0.2 M Na_2SO_4 at pH 3. For the EXAFS measurements, a solution with the free Y^{3+} ion (Y-sol) with a composition of 0.01 M $YCl_3·6H_2O$ at pH 4.6 and a solution of the YSO_4^+ complex (YSO_4-sol) with a composition of 0.01 M $YCl_3·6H_2O$ and 0.01 M Na_2SO_4 at pH 2.9 were prepared, respectively. Under these conditions, the major species in solution were Y^{3+} and YSO_4^+ (Figure S1). The yttrium concentrations of the references are listed in Table S1, and a more comprehensive description of the syntheses is given in the Supporting Information S1.

Waste Samples from Column Treatments. Column samples were collected from two laboratory column experiments of disperse alkaline substrate (DAS), as described in Ayora et al.,[12] simulating the remediation systems of the two AMDs from the Iberian Pyrite Belt region (SW Spain). The columns (9.6 cm in inner diameter and 39 cm in height) consisted of a permeable mixture of grained limestone and wood shavings at a 1:1 weight ratio. Samples W-MR-C1-4 and W-MR-C1-5 belonged to columns which treated AMD from Monte Romero mine, and the W-Alm-C3-8 and W-Alm-C3-9 samples belonged to columns which treated leaching of Almagrera mine tailing dam. Y concentration in different AMDs at the inlet ranged from 9 to 42 ppm, and sulfate concentrations were 3.5 and 11.7 mg/L. Physical-chemical parameters and water samples were collected every 2 weeks. Once the treatment was completed after 18 weeks, the solid was divided into 2 cm thick slices and dried. The partitioning of Al, Fe, and REEs was studied by performing a sequential extraction adapted from Torres and Auleda to the solid residues.[35] The results shown in Ayora et al. concluded that REEs were retained in basaluminite.[10] The W-MR-C1-4, W-MR-C1-5, W-Alm-C3-8, and W-Alm-C3-9 samples were selected from the depth where maximum Al concentration was extracted from the solids, assuming the solid slice that was the most enriched in basaluminite. These waste samples were used for EXAFS measurements, and the Y concentrations for these samples are shown in Table S2.

Analytical Techniques. Measurements of the pH values of the initial and final solutions were made with a Crison glass electrode calibrated with buffer solutions of pH 2, 4, and 7. The Al and S concentrations were measured by inductively coupled plasma (ICP) optical emission spectroscopy, and the Y concentration was measured by inductively coupled plasma mass spectrometry (ICP-MS). The aqueous speciation and saturation index of the solid phases were calculated with the PHREEQC code[36] using the Donnee Thermoddem_V1.10 database[37] provided by the Bureau de Recherches Géologiques et Minières (BRGM). Details of the analytical procedures and the database for the REE speciation are described in the Supporting Information S2.

The HEXS measurements were performed at the ID31 beamline at the European Synchrotron Radiation Facility (ESRF). The samples were loaded into 1.5 or 2 mm Kapton capillaries, and the HEXS patterns were obtained using a Pilatus3 X CdTe 2M detector. The data correction and generation of structure factors and pair distribution functions were performed with the PDFgetX3 software.[38] PDFs for aqueous solutions were obtained by subtracting the scattering signal of pure water from the total scattering signal of the YSO_4-sol sample and the Y-sol sample, respectively. The differential pair distribution functions (d-PDFs) for the B-Ycop sample were obtained by subtracting the PDF signal of a pure synthetic basaluminite from the PDF of the B-Ycop sample.

The EXAFS measurements of samples B-Yads, B-Ycop, A-Yads, Y-sol, and YSO_4-sol were performed at the Y K-edge (17.038 keV) at the FAME beamline,[39] BM30B, at the ESRF. The EXAFS measurements of the B-YSO_4 sample was performed at the Y K-edge (17.038 keV) at the CLÆSS beamline (ALBA synchrotron). Atomistic models of YSO_4^+ and Y^{3+} complexes adsorbed on a basaluminite surface with different initial configurations were employed in the data analysis to extract the Y local order parameters, including the neighbor distances, R, coordination number, N, and Debye–Waller factors, σ^2. The proportion of Y species present in each waste sample from column treatments was obtained by linear combination fitting (LCF) of the EXAFS spectra using the most representative reference compounds as the basis set. The experimental setup and the details of the data analysis are given in the Supporting Information S3.

The ab initio molecular dynamics (AIMD) simulations of an aqueous solution of yttrium(III) sulfate were carried out on a $Y^{3+}-SO_4^{2-}-OH^-$ system embedded in a box of 61 water molecules. The simulations were conducted with the electronic structure code, CP2K/Quickstep code, version 5.1.[40] CP2K implements density functional theory (DFT) based on a hybrid Gaussian plane wave. The revPBE generalized gradient approximations for the exchange and correlation terms were used together with the general dispersion correction termed DFT-D3.[41,42] The simulations were carried out for 15 ps in the canonical (constant NVT) ensemble to maintain the average temperature at T = 300 K. An in-house Python code using DiffPy-CMI was developed to convert the AIMD trajectories to PDF signals.[43] Details of the MD simulations are described in Supporting Information S4.

RESULTS AND DISCUSSION

Geometry of the Aqueous YSO_4^+ Complex. The experimental (YSO_4-sol, Y-sol) and theoretical (YSO_4-calc) PDFs of the Y-containing aqueous solutions, 0.1 M YNO_3 and YSO_4, are shown in Figure 1. Background subtraction of the aqueous samples was performed using a deionized water background, which implies that the experimental PDFs shown here are differential PDFs (water-subtracted). The background scale factor was adjusted to minimize the O–O correlation (~2.8 Å) in the PDFs. All spectra show an intense peak at 2.37 Å, which corresponds to the Y–O interatomic distances to oxygen in the first coordination shell. The experimental PDF of the YSO_4-sol sample shows a small and sharp peak at 1.45 Å, which corresponds unequivocally to the S–O interatomic distance in sulfate, and another smaller peak at ~3.6 Å, which is absent in the Y-sol sample. The DFT-based PDFs obtained from AIMD simulations of the YSO_4^+ aqueous complex also reproduced this latter peak. Analyses of the AIMD trajectories show that the 3.6 Å distance between Y and S is consistent with the formation of a monodentate inner-sphere complex (one shared oxygen) between the coordination shells of the sulfur and yttrium.

Fits of the EXAFS spectra of the aqueous solutions were performed using atomistic models from the AIMD simulations as initial structural models for the generation of the scattering paths. The results yielded an average Y–O distance of 2.37 ± 0.02 Å for the Y-sol sample and 2.38 ± 0.01 Å for YSO_4-sol (Table 1). The intense peak in the FT function at 2.38 Å for the two aqueous references represents the first solvation shell,

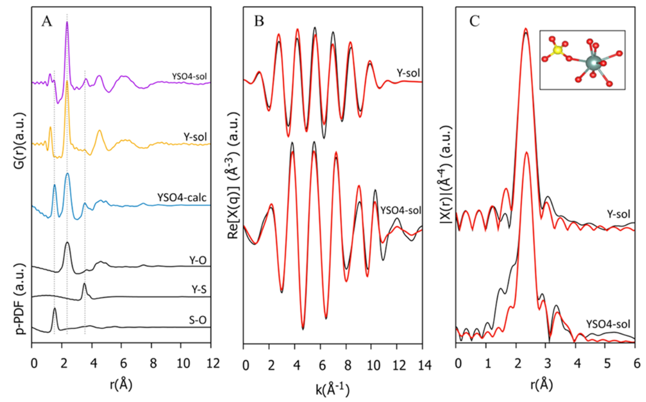

Figure 1. (A) Top: Experimental PDFs of the YSO_4-sol and Y-sol samples. Bottom: Simulated (AIMD) PDF (YSO_4-calc) and partial PDFs of a YSO_4^+ aqueous complex. (B) Fourier-filtered signal from 1.8 to 4.2 Å for the EXAFS data. (C) EXAFS Fourier transform (FT) amplitude functions of the YSO_4-sol sample. Black lines: experimental; red lines: fits. Simulated (AIMD) PDF and partial PDFs have been multiplied for visualization purposes: YSO_4-calc (3×), Y−S (5×), and Y−O and S−O (2×). Dashed lines indicate the position of the Y−O, Y−S, and S−O bonds in the YSO_4-sol sample.

and its asymmetry reveals a distribution of Y−O interatomic distances, as reported previously by Lindqvist-Reis et al.[24] The coordination numbers (CN) were 7.6 ± 1.9 and 7.9 ± 0.9 for Y-sol and YSO_4-sol, respectively, which are close to the expected value of 8 for HREEs. A second shell is visible in the FT of the YSO_4-sol sample. It was fitted with a Y−S distance of 3.50 ± 0.04 Å, similar to that observed in the PDF of the same sample, and a CN = 1. This corresponds to a monodentate coordination, matching the geometry obtained from the AIMD simulations. The coordination number CN = 1 was kept fixed in the EXAFS fitting to increase the stability of the fitting procedure, minimizing the number of parameters and excessive correlations between them. A multiple scattering path (Y−S−O) was included and was found to be relevant and to improve the fit. The fitting parameters matched both the PDF and modeling results and indicated that the YSO_4^+ aqueous species forms a monodentate inner-sphere complex.

The determined Y−O first shell coordination numbers and interatomic distances are consistent with those in previous reports describing yttrium coordination shells with $N = 8$ and Y−O distances of 2.36 Å.[23,24,28] Similar to aqueous REE carbonate and phosphate complexes,[31−33] aqueous Y−SO_4 ion pairs form inner-sphere complexes. This result contrasts with other ligands, such as chloride, which hardly form inner-sphere complexes at similar concentrations to those used in this study.[23] Only the formation of monodentate complexation between Dy and NO_3 with a distance of 3.57 Å has been reported using MD simulations.[26]

Local Order of Yttrium Adsorbed onto Basaluminite. HEXS measurements were performed on a pure basaluminite sample (B-pure) and on a sample of basaluminite coprecipitated with Y (B-Ycop). The PDFs are shown in Figure 2 with the differential PDF obtained by subtracting the PDF of the pure sample from that of the coprecipitated one. This approach has been previously used to examine the local order of different anions incorporated into poorly crystalline minerals, such as schwertmannite and basaluminite, and the desorption of sulfate from basaluminite when ageing at circumneutral pH values.[15,46] The PDFs of the two samples are similar and show characteristic basaluminite peaks that correspond to the known interatomic distances (S−O bond at ∼1.46 Å; Al−O bonds at 1.88, 4, 4.8, and 6 Å; and Al−Al bonds at 3 Å).[15,45] The differential PDF shows a main peak at 2.37 Å, which corresponds to the Y−O distance. This peak matches the distance from Y to the first solvation shell obtained from the EXAFS and PDF of the Y^{3+} and YSO_4^+ aqueous solutions (Figure 1). Another peak is present at 1.7 Å, which is tentatively assigned to a new Al−O distance of the Al-octahedra, due to probable distortions of the basaluminite. The existence of deformations in the structures of mineral nanoparticles upon oxyanion adsorption has been previously observed.[44,46] A smaller peak appears at 3.48 Å, which can be tentatively assigned to a Y−S distance, though it is shorter than the Y−S distance reported for the YSO_4^+ aqueous complex (Table 2 and Figure 1A). This peak may also correspond to a Y−Al interatomic distance, which would be consistent with the formation of an inner-sphere ligand, as suggested by Lozano et al.[17] This hypothesis will be tested using different atomistic models for the fitting of the EXAFS data. Other peaks at longer distances are difficult to assign in the absence of a more detailed structural model.

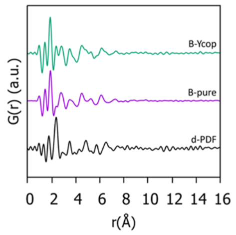

Figure 2. PDFs of basaluminite coprecipitated in the presence of Y (B-Ycop) and pure basaluminite (B-pure) and differential PDF (d-PDF). The d-PDF spectrum has been amplified (3×) for visualization purposes.

The k^3-weighted EXAFS spectra for the solid references, B-YSO_4-ads, B-Y-ads, B-Y-cop, and A-Y-ads (Figure 3), are indistinguishable and differ from the aqueous Y-sol and YSO_4-sol spectra in that a slight oscillation becomes visible at 5−6 $Å^{-1}$. In B-YSO_4-ads, the dominant Y species in solution is the YSO_4^+ complex. However, in B-Y-ads, B-Ycop, and A-Yads, the dominant Y species is Y^{3+}. Still, these four samples show similar spectra. Since the common feature in these three samples is the

Table 1. Modeling Parameters of the Y K-Edge EXAFS Spectra of the 0.1 M YSO_4 Aqueous Solution[a]

sample	neighbor	path	N	σ^2	ΔE_0	R (Å)	Var.	χ_ν^2
Y sol	1st shell	Y−O	7(2)	0.005(3)	−2(3)	2.37(2)	4	354
Y−SO_4 sol	1st shell	Y−O_1	7.9(9)	0.007(2)	−1(1)	2.38(1)	8	498
	2nd shell	Y−S	1_{fixed}	0.003(6)		3.50(4)		
	3rd shell	Y−S−O	1_{fixed}	0.015(19)		3.18(10)		

[a] The error is expressed in parentheses after the last digit.

Table 2. Results of the EXAFS Fits for the B-YSO$_4$ Reference[a]

model	neighbor	path	N	σ^2	ΔE_0	R	Var.	χ_ν^2
1*	1st shell	Y−O$_1$	6_{fix}	0.007(1)	−3(2)	2.32(1)	9	338
		Y−O$_2$	2_{fix}	0.004(8)	−3(2)	2.47(2)		
	2nd shell	Y−S	1_{fix}	0.008(5)	−3(2)	3.33(4)		
		Y−Al	2_{fix}	0.012(5)	−3(2)	3.52(5)		
2	1st shell	Y−O	10(1)	0.012(2)	−6(2)	2.33 (1)	8	402
	2nd shell	Y−S	1_{fix}	0.009(5)	−6(2)	3.88 (5)		
		Y−Al	1_{fix}	0.006(3)	−6(2)	3.42 (3)		
3	1st shell	Y−O	10(1)	0.013(1)	−4(1)	2.33(1)	8	334
	2nd shell	Y−S	1_{fix}	0.008(3)	−4(1)	3.34(3)		
		Y−Al	2_{fix}	0.011(5)	−4(1)	3.92(4)		

[a] Model 1: monodentate inner sphere. Model 2: bidentate mononuclear inner sphere. Model 3: bidentate binuclear inner sphere. Var. indicates independent variables. The best model is indicated with an asterisk (*). The error is expressed in parentheses after the last digit.

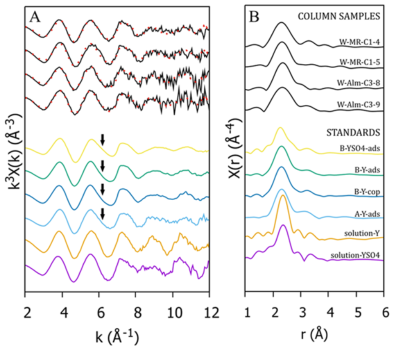

Figure 3. k^3-Weighted EXAFS (A) and FT amplitude functions (B) for four waste samples from column treatments, W-MR-C1-3, W-MR-C1-4, W-Alm-C3-8, and W-Alm-C3-9 (upper part); solid standards (basaluminite sorbed with YSO$_4$ (B-YSO$_4$), basaluminite sorbed and coprecipitated with Y: B-Yads and B-Ycop, respectively); and aqueous solution (free ion and sulfate complex: Y-sol and YSO$_4$-sol, respectively) (bottom part). The dashed lines in the EXAFS signals of the column samples represent LCF with B-Yads (basaluminite with sorbed yttrium) and YSO$_4$-sol (solution of Y with SO$_4$) standards as the most representative references (results in Table 3). The arrows indicate a frequency present in the solid standards.

presence of an Al adsorbent, and this feature agrees with that in the B-YSO$_4$-ads EXAFS spectrum, we hypothesize that the higher frequency observed at 5−6 Å^{-1} (arrow in Figure 3) may be related to the presence of an Al backscatterer, rather than to a signal from a close sulfate group. Both Al and S are light atoms with similar atomic numbers (Z = 13 and 16, respectively), which makes their backscattering functions difficult to distinguish via fitting of the EXAFS signal. These observations lead us to assume that the EXAFS measurements have poor sensitivity to the presence of Y−S bonds in this system. However, a contribution from a sulfate shell for the first two samples cannot be ruled out.

Based on the previous information of the aqueous species and on the thermodynamic model of REE sorption,[17] the B-YSO$_4$-ads EXAFS signal was fitted with three models of different geometries of the YSO$_4^+$ aqueous complex adsorbed onto basaluminite surfaces via inner-sphere complexes (Figure 4), to obtain an atomistic model representation: (A) a monodentate surface complex, (B) a bidentate mononuclear surface complex, and (C) a bidentate binuclear surface complex.

The EXAFS fits for B-YSO$_4$-ads for the different models and the calculated parameters are given in Figure 5 and Table 2, respectively. The first model represents a monodentate inner-sphere surface complex. The coordination number of the shells has been fixed based on information from other sources: the major aqueous species in solution is YSO$_4^+$, which, as supported by PDF and DFT data, forms a monodentate aqueous complex. Besides, the thermodynamic model of REE sorption on basaluminite indicated monodentate complexation of the YSO$_4^+$ aqueous complex.[17] With this information, the fit

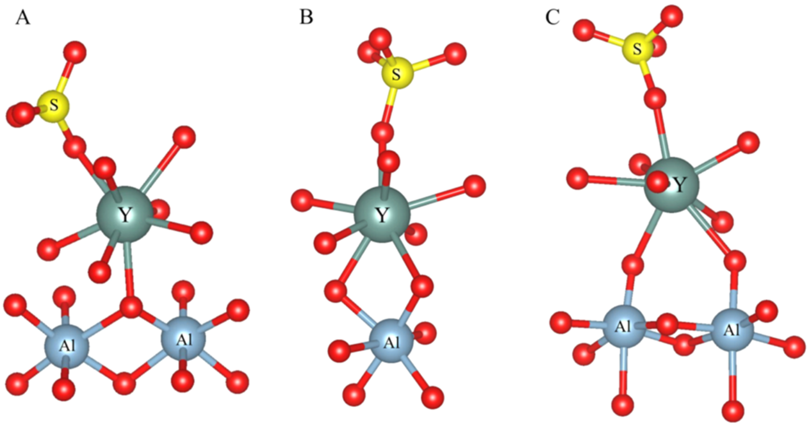

Figure 4. Atomistic representations of the three models of YSO$_4$ aqueous complexes adsorbed on the basaluminite−water interface. The different atomic positions of YSO$_4$ to octahedral-Al are used to fit the EXAFS signal of the B-YSO$_4$ sample. The three models show different inner-sphere surface complexes: (A) monodentate, (B) bidentate mononuclear, and (C) bidentate binuclear.

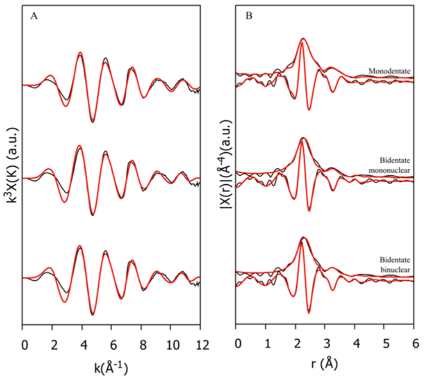

Figure 5. (A) k^3-Weighted EXAFS spectr[illegible] the Y K-edge of the basaluminite with YSO_4 sorbed (B-YSO[illegible]erence) and (B) its Fourier transform amplitude. The experimental and fitted curves are shown in black and red, respectively.

was performed assuming S and Al coordination numbers equal to 1 and 2, respectively, as is shown in Figure 4A. Besides, two oxygen paths were considered due to the Y−O length variation improving the fit. Thus, the fit yielded a first coordination shell with a Y−O distance range between 2.32 and 2.47 ± 0.02 Å with a fixed coordination number of 8. The second shell was fitted yielding a Y−Al distance of 3.52 Å, with a fixed coordination number of $N = 2$, and a Y−S distance of 3.33 Å, with a fixed number of $N = 1$. This result is consistent with the monodentate inner-sphere complex of Y with one oxygen shared with two surface Al sites (Figure 4A). The second model, the bidentate binuclear inner-sphere complex configuration, gave poorer results without structural significance and with higher χ_ν^2 values (Table 2), so it was discarded. The third model was the bidentate binuclear complex; the first shell was fitted with a coordination number of 10 ± 1.31 and a distance of 2.33 Å. The second shell was fitted with a S path yielding a Y−S distance of 3.34 Å with a fix coordination number of $N = 1$, similar to that for the monodentate hypothesis, and with an Al path with a fixed coordination number of $N = 2$ giving a bit longer distance of 3.92 Å.

Overall, the monodentate inner-sphere surface complex gave the best fit results, which was in accordance with the thermodynamic sorption model. Moreover, the bidentate binuclear inner-sphere surface complexes also yielded a good fit with similar χ_ν^2 values to those of the monodentate hypothesis, making this configuration also possible (Figure 4C). In both fits, the distances between Y−S are similar, 3.33 and 3.34 Å, which is also observed in the differential PDF of the B-Ycop reference. From the EXAFS data, the presence of a bidentate binuclear surface complex cannot be ruled out. However, the thermodynamic modeling and the EXAFS data both agree on the monodentate surface complex being the one present at the basaluminite−water interface.

The EXAFS of the B-YSO_4-ads standard was also fitted with the same three atomistic models presented in Figure 4 but without sulfate included (Figure S2) to analyze the sensitivity of the fit to the presence of sulfate. The Al−O distances obtained with these new fits (Table S3) were almost identical to those calculated when including sulfate shells (Table 2), with the exception in the monodentate inner-sphere configuration, which was a bit longer. Thus, the presence of Al is consistent in the two models, with and without sulfate. However, the fits obtained with the sulfate group included showed lower values of the agreement factor (reduced chi-square) (compare Tables 2 and S3). This discussion highlights the difficulties of the EXAFS technique to discern the presence of low-Z backscatterers, in particular in disordered systems such as the one present here.

These results are consistent with those presented by Rabung et al., where Gd and Lu were shown to adsorb onto γ-Al_2O_3 to form inner- sphere complexes.[47] Lu, which is considered a HREE as Y, was shown to form a monodentate surface complex with a first shell of 7 atoms and a Lu−O distance of 2.28 Å. The longer Y−O distance found here for Y is consistent with its larger Y ionic radius. However, these authors could not detect any Lu−Al bonds in their EXAFS data. Other sorption studies of Eu onto γ-Al_2O_3 showed the formation of both monodentate and bidentate binuclear complexes.[20] In contrast to this study and to the results of Rabung et al. on Al oxides, EXAFS studies of lanthanides sorbed onto ferric oxides have shown a predominance of bidentate inner-sphere complexes.[47] Lu adsorbed onto ferrihydrite at pH ≥ 5.5 yielded an Lu−O coordination number of 7 at a distance of 2.30 Å, and a second coordination shell was identified with a Lu−Fe interatomic distance of 3.38 Å. These EXAFS results were complemented by time-resolved laser fluorescence spectroscopy measurements that showed five water molecules surrounding the metal cations, which was interpreted as a bidentate inner-sphere complex.[22] The similar distance to the second shell found by Dardenne et al.[22] and by us in these two different systems can be explained by the smaller size of Lu in comparison to that of Y, which is compensated for by the longer Fe−O bond distance in comparison to the Al−O bond, making possible a bidentate mononuclear sphere at 3.4 Å in Fe oxides and Al oxides. Another study by Estes et al. reported Eu K-edge EXAFS data of Eu(III) sorbed onto hematite.[19] They observed a decrease in the coordination number of the Eu−O bond from 8 to 5 upon adsorption accompanied by a smaller Eu−Fe bond distance of 3 Å. This result was interpreted via molecular simulations as being due to the formation of an inner-sphere bidentate mononuclear surface complex. Such a decrease in the coordination number was not observed in this study; the CN of the Y−O correlation was maintained at ∼8 ± 1 for both the aqueous and surface complexes.

Identification of Y Species in Waste Samples from AMD Treatment. The k^3-weighted EXAFS of the column samples (upper part) and standards (lower part) and their Fourier transform (FT) envelope functions with corrected phase shifts are shown in Figure 3. Visual comparisons of the EXAFS spectra of the column samples reveal a strong similarity between them, suggesting similar local order of Y in all samples. In addition, the EXAFS spectra of the column samples are very similar to those of the solid references (B-YSO_4-ads, B-Y-ads, B-Y-cop, and A-Y-ads). They have a shoulder at ∼6.5 Å^{-1}, indicating a higher frequency, which is absent in the aqueous samples (see the arrow in Figure 3).

Based on the PCA analyses (see Chapter S3), the reconstructed spectra indicated that only two components were required to describe the samples (Figure S4). The two most likely Y species identified by target transformation of the standard spectra were the B-YSO_4-ads and B-Y-ads references (Figure S5). However, since their EXAFS signals are very similar, LCF of the EXAFS spectra of the waste samples from column treatments was performed using B-YSO_4-ads and YSO_4-sol (Figure 3A, upper part) to quantify the proportions of different Y species in the waste samples. The use of these

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Table 3. Percentages of Y Species in the Column Samples Obtained from LCF of the EXAFS Spectra. *R*-Factor and χ^2 Are Defined in Chapter S3 of the SI

standard	C1-4	C1-5	C3-8	C3-9
B-YSO_4ads	0.719 ± 0.036	0.867 ± 0.038	0.495 ± 0.059	0.746 ± 0.061
YSO_4-solution	0.281 ± 0.069	0.133 ± 0.071	0.505 ± 0.084	0.254 ± 0.085
R-factor	0.14	0.14	0.29	0.30
$\chi2$	133	154	371	392

two standards would correspond to YSO_4^+ adsorbed forming inner- and outer-sphere complexes, respectively.

The LCF results show that more than 75% of Y adopts a local geometry similar to that of the B-YSO_4-ads reference (with the exception of sample W-Alm-C3-8, for which the LCF indicated equal proportion of both YSO_4 presented as inner- and outer-sphere complexes (Table 3)). The waste samples were selected from the depth where the major proportion of Al precipitated, assuming basaluminite precipitation. However, other minor mineral species may have also been precipitated, such as Fe-oxyhydroxysulfate, due to the presence of a small amount of Fe in the solids. Specifically, samples from the Almagrera column (W-Alm-C3-8 and W-Alm-C3-9) presented higher Fe concentration than samples from Monte Romero treatment. REEs can also be scavenged by amorphous Fe hydroxides in AMD neutralization environments,[48] so a minor or almost negligible fraction of Y could be retained by the small proportion of ferric oxides precipitated in the selected samples, explaining the lower proportion of B-YSO_4-ads.

■ ENVIRONMENTAL IMPLICATIONS

The YSO_4^+ aqueous species has been characterized combining PDF analyses of aqueous solutions and AIMD simulations, confirming the formation of an inner-sphere Y−SO_4 ion pair with a monodentate configuration, with a Y−S interatomic distance of 3.5 Å. Results from the thermodynamic sorption model describe REE sorption onto basaluminite via sorption of aqueous $REESO_4^+$. The use of an atomistic model using this positively charged ion yields the best results for the EXAFS fitting of Y sorbed on basaluminite. However, the EXAFS technique cannot confirm the presence of YSO_4^+ sorbed onto basaluminite by itself, due to the low sensitivity to discern between Al and S neighbors. However, the EXAFS fitting, together with the PDF, can confirm the strong interaction and the formation of inner-sphere surface complexes of Y on basaluminite precipitates, via ligand exchange with AlO_6 units of its structure. EXAFS analyses of column waste samples show that most of the Y is retained as the same inner-sphere sorbed species, YSO_4^+, with a low proportion of YSO_4^+ in the outer-sphere configuration.

The description of the local structure of yttrium sorbed onto the basaluminite surface provided here complements the atomic configuration studies of other trace metals, such as As and Se oxyanions.[44] The chemical similarity between yttrium and other HREEs (from Tb to Lu) suggests that similar environments could be present for the other elements of the same group. This fact has important environmental consequences, as the HREE would be strongly sorbed, via covalent bonds, which could result in their long-term immobilization at least until the host phase is dissolved or re-precipitated. A key question emerges about the long-term stability of the complex, particularly with an increase in the solution pH. The structural evolution of pure basaluminite with increasing pH showed its recrystallization onto boehmite, releasing sulfate into the solution.[45] Previous studies on poorly crystalline Fe phases from AMD, such as schwertmannite, have shown a release of adsorbed toxic elements during aging due to recrystallization processes.[49] The occurrence of such processes in REE-doped basaluminite could result in the remobilization of REEs and of other potentially adsorbed toxic elements. The extent to which these processes can occur in natural waters requires further investigation.

Further studies on the potential uptake of LREEs by basaluminite are necessary to confirm and/or compare different structural mechanisms to those of their HREE counterpart, as a step to develop separation methods for REEs. These investigations will help enhance a selective recovery of REEs from AMD wastes and thus to generate an economic value of the waste generated during the neutralization of AMD-affected waters.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b01795.

> Synthesis of reference materials, analytical procedures and aqueous speciation calculations, synchrotron experiments and data analyses, molecular dynamics simulations, and the Phyton code used to generate PDF from AIMD simulations; samples used for EXAFS measurements and the modeling parameters from EXAFS fitting; and illustrating fitting of EXAFS spectra (PDF)

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Notes

The authors declare no competing financial interest.

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Solid and aqueous speciation of yttrium in passive remediation systems of acid mine drainage

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Supporting Information

The Supporting information contains 19 pages, 3 tables and 5 figures.

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S1 SYNTHESIS OF REFERENCE MATERIALS

Basaluminite was synthesized following the method described by Adams and Rawajfih[1]. A solution of 214 mL of 0.015 M $Ca(OH)_2$ was added drop-by-drop to 30 mL of 0.05 M $Al_2(SO4)_3\cdot 18H_2O$ (both commercial reagents) while being stirred until an OH:Al ratio of 2.14 was reached. The solid was washed three times to remove coprecipitated $CaSO_4\cdot 2H_2O$ and dried for 48 hours at 40°C.

Nanoboehmite was synthesized following the method described by Xu et al.[2]. A solution of 0.5 M $AlCl_3\cdot 6H_2O$ was mixed with 1 M NaOH. The titration was conducted drop-by-drop until reaching a pH of 8.1. The precipitate was washed three times with deionized water and dried for 72 hours at 40°C.

X-ray diffraction analyses were performed to ensure the purity of the samples. Digestions of 0.1 g of solids in 5 mL HNO_3 65% were carried out for 12 hours at 115°C for chemical characterization.

S2 DETAILS OF ANALYTICAL PROCEDURES AND AQUEOUS SPECIATION CALCULATIONS

Measurements of pH values were made with a Crison® glass electrode calibrated with buffer solutions of pH 2, 4, 7 and 9. Concentrations of major cations (S and Al) were measured by ICP-AES (Thermo Scientific – iCAP 6500, Radial acquisition) and Y was determined ICP-MS (Perkin-Elmer®SciexElan 6000). The detection limits were 1.6 and 1.0 μmol/L for S, Al and 0.2 μg/L for Y, respectively. Certified solutions (CPI International-CCV standard 1-solution A) were intercalated within the samples to check the analytical accuracy. The analytical precision error was estimated to be approximately 2% for ICP-AES and ICP-MS measurements. Two AMD laboratory standards supplied by P. Verplank (USGS), were also analyzed for REE accuracy, giving deviations lower than 5% of the recommended values, with the exception of Eu, giving values 25% below the recommended value[3].

The Donnee Thermoddem_V1.10.dat database[4] has been updated with the stability constants at zero ionic strength and 25°C for the following inorganic complexes for lanthanides and yttrium: $LnCO_3^+$, $LnCO_3^{-2}$ and $LnHCO_3^{+2}$ [5]; $LnSO_4^+$ [6]; $LnOH^{+2}$ [7], $LnOH_2^+$, $LnOH_3$ [8]; $LnCl^{+2}$, $LnCl_2^+$ [9]; LnF^{+2}, LnF_2^+ [10]; and $LnNO_3^{+2}$ [11] . Solubility products for REE $Ln(OH)_3$ and $Ln(OH)_{3(am)}$ solids have been complemented with those from the LLNL database (Johnson et al., 2000) and with those reported by Spahiu and Bruno[12] Scandium aqueous complexes, $Sc(OH)^{+2}$, $Sc(OH)_2^+$, $Sc(OH)_3$, $ScSO4^+$; and the solubility product for $Sc(OH)_3$ by Wood and Samson[13] were incorporated as well to the database. The aqueous speciation and saturation index of the solid phases were calculated with the PHREEQC code[28] using the Donnee Thermoddem_V1.10 database.

S3 SYNCHROTRON EXPERIMENTS AND DATA ANALYSES

S3.1 Pair Distribution Function analyses

HEXS measurements were performed at beamline ID31 at the European Synchrotron Radiation Facility (ESRF). Powder samples were loaded into polyamide capillaries. The samples and background measurements were performed at room temperature with incident X-rays of 70 KeV (λ=0.177 Å). The incident X-ray energy was calibrated using a CeO_2 standard (NIST 674b). The 2D images were collected with a flat panel Pilatus3 X CdTe 2M detector. The obtained images were corrected and integrated using pyFAI[14]. Structure factors, S(Q), and pair distribution functions, PDFs, were obtained using the PDFgetX3 software[15]. Differential pair distribution functions (d-PDFs) were obtained by subtracting the PDF signal of pure synthetic basaluminite from the PDF of Y-doped basaluminite. Background subtraction of the aqueous samples was performed using a deionized water background. The background scale factor was adjusted to minimize the O-O correlation (~2.8 Å) in the PDFs.

S.3.2 EXAFS analyses

The EXAFS measurements of aqueous and solids B-Yads, B-Ycop, A-Ycop solid samples were performed at the Y K-edge (17.038 keV) on the FAME beamline[16] (the French bending magnet beamline, BM30B, at the ESRF), and B-YSO4-ads and Y_2O_3 sample on CLÆSS beamline (wiggler absorption beamline at the national Spanish light source, ALBA[17]). At Fame the X-ray optics configuration consisted of a pair of vertically focusing Rh-coated mirrors inclined at 2.7 mrad, providing harmonics rejection and vertical focusing. The monochromator was a cryogenically cooled and dynamic sagittal focusing double crystal monochromator equipped with a pair of Si(220) crystals. The beam size at the sample was approximately 100 × 200 μm^2 (vertical × horizontal). The energy calibration was performed at the first peak in the first derivative of the absorption spectrum of a Y foil and monitored with the same reference foil mounted in transmission after the sample. The incoming and transmitted beams were monitored with photodiodes reading the scattered signal from the X-rays passing through air-filled chambers. The partial fluorescence yield was measured with an energy dispersive high-purity Ge detector with thirty elements that was mounted at 90° on the scattering plane to minimize parasitic scattering. The strong fluorescence signal coming from the matrix of the samples was filtered with 150-μm-thick Al foil and a Sr filter of three absorption lengths. The measurements were performed at 20 K in a liquid He flow cryostat to reduce thermal vibrations (enhancing the EXAFS signal) and to avoid radiation damage. The spectra were acquired for approximately 40 minutes and repeated three to four times to obtain optimal statistics.

Room temperature EXAFS Spectra of B-YSO4-ads and, Y_2O_3, samples have been collected in transmission mode at CLÆSS beamline. This is the optical scheme of the beamline. The synchrotron radiation emitted by the multi-pole wiggler is first collimated vertically by the first mirror and then monochromatised using a liquid nitrogen cooled Si (311) double crystals monochromator. The x-ray beam is finally focused down to the sample at about 500 μm x 500 μm (H x V) by changing the radius of curvature of the second vertically focusing mirror. The incoming and outgoing photon fluxes have been measured by ionization chambers filled with an appropriate mixture of N2 and Kr gases. Beamline energy was calibrated on the edge position of the Y_2O_3 spectrum[18].

The solid samples were prepared as 5-mm-diameter pellets after fine grinding and diluting with BN. They were mounted on a PEEK (polyether ether ketone) sample holder and sealed with Kapton film. Frozen samples were prepared by depositing the aqueous solution onto the sample holder, which was kept in liquid nitrogen vapor, sealed with Kapton film and kept in liquid N_2 until being mounted in the cryostat. All of the column samples, A-Yads reference and aqueous solutions were measured in fluorescence mode, whereas the Y reference compounds were measured in transmission mode. Multiple scans (3-5) were taken from each sample to obtain good statistics and signal-to-noise for EXAFS analysis. Each scan was checked for energy calibration and then a mean of 4 scans were merged.

The data reduction, normalization and EXAFS extraction were performed following the standard protocols implemented in the Athena software[17]. Normalization was performed using a linear pre-edge function and a second-order post-edge polynomial. The pre-edge and post-edge normalization range were,-150 to-30 eV and from 150 to 744 eV, respectively. The normalization used a linear pre-edge function and a quadratic post-edge polynomial. The EXAFS spectra were analyzed using the Athena software with two different procedures.

Principal component analysis (PCA) of the four EXAFS spectra obtained from the waste samples was performed in a k range of 3-12 $Å^{-1}$. The PCA determines the number of components that reproduces the EXAFS spectra for the set of column samples with the standards. The criterion used to estimate the number of species representative of each spectrum was to obtain a decrease in the R value of 20%, where R is defined as:

$$R = \frac{\sum_{i}^{N_{fit}} \left[\chi_i^{data} - \chi_i^{model}(x)\right]^2}{\sum_{i}^{N_{fit}} \left[\chi_i^{data}\right]^2}$$

where N_{fit} is the number of data points, X is the set of variables, Є is the noise level of the data, and N_{idp} is the number of independent data points.

This criterion was also checked by visual examination of the reconstructed spectra. Fig. S4 shows the experimental spectra reconstructed with combinations of two and three principal components (dashed lines). The first two components reproduce each spectrum reasonably well. Introducing a third component into the spectra gives a better reconstruction (improvement in R greater than 20%); however, the improvement to the fit is mostly in the k range > 9 $Å^{-1}$, where the signal is very noisy. Therefore, two components were considered to reproduce the experimental spectra satisfactorily.

After the examination of the components, the target transformation operation was performed to evaluate which references were the principal components. The two references with the lowest χ^2 values were B-Yads and B-Ycop, followed by A-Yads (Fig. S5). These three EXAFS spectra are nearly identical, and since basaluminite is amorphous, the yttrium geometry is expected to be the same in both solids. Thus, B-Yads and the following better reference, YSO4-sol, were selected, which represent yttrium attached to basaluminite as an inner sphere ligand and yttrium as a YSO_4^+ outer sphere ligand, respectively.

Linear combination fitting (LCF) was performed for each EXAFS spectrum of the waste samples with the B-Yads and YSO4-sol standards. The fraction of each standard spectrum is proportional to the amount of this species in the waste solid from the column treatments; thus, this result identifies the Y species in these solids. The precision of the fit is expressed by the error factor χ_v2, which is defined as:

$$\chi_v^2 = \frac{\chi^2}{(N_{idp} - N_{varys})}$$

where Nidp is the number of independent data points, Nvarys is the number of variables, and χ2 is defined as:

$$\chi^2 = \frac{N_{idp}}{\epsilon^2 N_{fit}} \sum_{i}^{N_{fit}} [\chi_i^{data} - \chi_i^{model}(x)]^2$$

The Artemis software[19] was used to estimate the backscattering phases and amplitude functions of the scattering paths. Atomistic models of aqueous solutions containing the YSO_4^+ complex were built from snapshots obtained from the molecular dynamics simulations. Atomistic structures of Y^{3+} adsorbed onto the AlO_6 octahedra from basaluminite were built from the structural model of basaluminite[20]. The K^3-weighted EXAFS spectra were fit in the range of 2.46-10.71 $Å^{-1}$. The coordination number (N), interatomic distance (R), Debye-Waller factor (σ^2) and ΔE_0 for the samples were allowed to vary and were linked to all of the shells during the fit. The goodness of the fit was evaluated by χ_v^2.

S4 MOLECULAR DYNAMICS SIMULATIONS

Ab initio (Born-Oppenheimer) molecular dynamics (AIMD) simulations were conducted with the electronic structure code CP2K/Quickstep, version 5.1[21]. CP2K implements DFT based on a hybrid Gaussian plane wave. Several studies have shown that generalized-gradient DFT approximations give radial distribution function for liquid water that are overstructured compared with experiments[22]. In this study, the revised Perdew–Burke–Ernzerhof (revPBE)[23] functionals were therefore augmented with the Grimme's dispersion correction termed DFT-D3[24]. The inclusion of van der Walls corrections to GGA functionals leads to a softer liquid structure[25,26]. Goedecker-Teter-Hutter pseudopotentials[27] were used to describe the core–valence interactions. All atomic species were represented using a double-zeta valence polarized basis set. The plane wave kinetic energy cut off was set to 1000 Ry. The *k*-sampling was restricted to the Γ point of the Brillouin zone. Simulations were carried out with a wave function optimization tolerance of 10^{-6} au that allows for 1.0 fs time steps with reasonable energy conservation. Periodic boundary conditions were applied throughout. AIMD simulations were carried out in the canonical (constant NVT) ensemble using a Nosé-Hoover chain thermostat to maintain the average temperature at T = 300K. AIMD of an aqueous solution of Yttrium(III) sulfate were carried out on a Y^3 – SO_4^{2-}–OH^- system embedded in a box of 61 water molecules. The initial configuration was generated starting from the last configuration of 200 ps of classical simulation of 64 water molecules in the isothermal–isobaric (T = 300 K and P = 1 atm) ensemble, which resulted in a equilibrated volume with cell vectors $\vec{a}$= (12.285, 0.000, 0.000), $\vec{b}$= (0.000, 12.285, 0.000), and $\vec{c}$= (0.000, 0.000, 12.285) (in Angstrom). Starting from the last configuration, one H_2O molecule was substituted with one Y^{3+}, and we conducted 40 ps of AIMD simulations. Finally, two H_2O molecules coordinated with Y^{3+} were substituted with one SO_4^{2-} and one OH^- ion, and we conducted further 15 ps simulations.

Pair Distribution Functions (PDF) and partial PDFs were generated from the AIMD trajectories using a home-built python code that makes use of the DiffPy-CMI library[28]. In order to minimize the contribution of bulk water and to be able to compare with the water-subtracted experimental PDFs of the aqueous YSO_4^+ complex, the O-O correlations were not included in the calculations.

S5 PYTHON CODE TO GENERATE PDF FROM AIMD SIMULATIONS

```
##################################################
## {Code to calculate PDFs from MD simulations
## (collection of snapshots in xyz format) using diffpy}
##################################################
## Author: {AlexFM}
## Copyright: {2019}, {Collaboration with IDAEA, EMPATIA project}
## Version: {1.0 Feb 2019}
## Email: {Alex.Fernandez-Martinez@univ-grenoble-alpes.fr}
##################################################
#


import numpy as np
import matplotlib.pyplot as plt
from diffpy.Structure import loadStructure, Lattice
from diffpy.srreal.pdfcalculator import DebyePDFCalculator
from diffpy.srreal.pdfcalculator import PDFCalculator

dpc = DebyePDFCalculator()
pc=PDFCalculator()


#Define parameters for PDF calculations
filename_experimental_pdf="
filename_output="

nframes=50000
pc.qmin=2
pc.qmax=25
pc.rmax=25
pc.qdamp=0.3

pc.setTypeMask('H','H',False)  #eliminates this pair
pc.setTypeMask('H','O',False)  #eliminates this pair
pc.setTypeMask('H','Y',False)  #eliminates this pair
pc.setTypeMask('H','S',False)  #eliminates this pair
pc.setTypeMask('O','Y',False)  #eliminates this pair
pc.setTypeMask('O','O',False)  #eliminates this pair
pc.setTypeMask('Y','Y',False)  #eliminates this pair
pc.setTypeMask('S','Y',False)  #eliminates this pair
pc.setTypeMask('O','S',True)   #includes this pair
pc.setTypeMask('S','S',False)  #eliminates this pair

#Read file containing MD trajectory
f = open('y_so4_m_oh_61w-pos-1.xyz', "r")
lines=f.readlines()
print 'lines read'
lines2=[]
for i in lines:
        j=i[:-1]
        lines2.append(j)
print 'lines corrected'

i=0
sizef=np.shape(lines)[0]
grall=[]

#Create lattice
```

```
box=Lattice(12.28519616,12.28519616,12.28519616,90,90,90)

while i<nframes:
    xyz=lines2[i:i+193]
    np.shape(xyz)
    np.savetxt('test.xyz',xyz,fmt='%s')
    cluster=loadStructure('test.xyz')

    #cluster.Uisoequiv=0.008
    for j in np.arange(cluster.element.shape[0]):
    #print cluster.element[i]
        if cluster.element[j]=='O':
                            #print cluster.element[i]
            cluster[j].Uisoequiv=0.015
                            #print cluster.Uisoequiv[i]
        elif cluster.element[j]=='Y':
                            #print cluster.element[i]
            cluster[j].Uisoequiv=0.001
                            #print cluster.Uisoequiv[i]
        elif cluster.element[j]=='S':
                            #print cluster.element[i]
            cluster[j].Uisoequiv=0.005
              #print cluster.Uisoequiv[i]
              cluster[187].Uisoequiv=0.005
              cluster[188].Uisoequiv=0.005
              cluster[189].Uisoequiv=0.005
        cluster[190].Uisoequiv=0.005
    cluster.placeInLattice(box)  #Place cluster in lattice
    r1, g1 = pc(cluster)
    grall.append(g1)
    #plt.plot(r1,g1)
    i=i+193
    print i


grall2=np.asarray(grall)
YSO4=np.loadtxt(filename_experimental_pdf,skiprows=27).T

#Plot results together with experimental PDF
plt.plot(YSO4[0],YSO4[1]*0.5,label='experimental')
plt.plot(r1,grall2.mean(axis=0),label='calculated')
plt.legend()
plt.show()

#Output to ascii file
np.savetxt(filename_output,np.transpose([r1,grall2.mean(axis=0)]))

f.close()
```

Table S1. Description of aqueous and solid standards. Type of synthesis, Y concentration in ppm and acquisition mode for EXAFS measurements.

Sample	mineral	Synthesis	ppm	Mode
B-YSO4-ads	Basaluminite	YSO4-adsorbed	20000	Transmission
B-Yads	Basaluminite	Y-adsorbed	20000	Transmission
B-Ycop	Basaluminite	Y-coprecipitated	80000	Transmission
A-Yads	Amorphous $Al(OH)_3$	Y-adsorbed	280	Fluorescence
Y-sol	1000 ppm Y, pH 4.6	Y aqueous	1000	Fluorescence
YSO4-sol	1000 ppm Y, 2000 ppm SO_4 (Na_2SO_4) , pH 3	Y aqueous	1000	Fluorescence

Table S2. Description of column samples, Y concentration and acquisition mode for EXAFS measurements.

Sample	Part of colum	AMD Mine	Y ppm	EXAFS acquisition mode
W-MR-C1-4	Column Matrix	Monte Romero	37.5	Fluorescence
W-MR-C1-5	Column Matrix	Monte Romero	42.0	Fluorescence
W-Alm-C3-8	Column Matrix	Almagrera	7.8	Fluorescence
W-Alm-C3-9	Column Matrix	Almagrera	9.8	Fluorescence

Table S3. Modeling parameters for Y K-edge EXAFS in YSO$_4^+$ sorbed basaluminite sample (B-Yads) but taking into account free yttrium, Y^{3+}, at different inner sphere positions 1) Y as monodentate inner sphere ligand, 2) Y ion as bidentate mononuclear inner sphere ligand, and 3) Y ion as bidentate binuclear inner sphere ligand.

Sample	Model	path	N	σ^2	ΔE_0	R	Var.	χ_ν^2
B-YSO4-ads	1. Monodent.	Y-O	9(1)	0.012 (1)	-5(1)	2.34 (1)	6	884
		Y-Al	2_{fix}	0.010 (3)	-5(1)	3.43(3)		
	2. Bident. Mononuc.	Y-O	9(1)	0.013 (1)	-6(2)	2.33(1)	6	481
		Y-Al	1_{fix}	0.006 (4)	-6(2)	3.42 (4)		
	3. Bident. Binuc.	Y-O	11(2)	0.014 (1)	-5(2)	2.33(1)	6	514
		Y-Al	2_{fix}	0.011 (6)	-5(2)	3.92(5)		

Figure S1. Y Aqueous speciation for aqueous solutions of (A) 0.1 M $Y(NO_3)_3$, (B) 0.1 M $Y(NO_3)_3$ plus 0.1 M Na_2SO_4, (C) 0.01 M YCl_3 and (D) 0.01 M YCl_3 plus 0.01 M Na2SO4, respectively, at pCO_2 3.5.

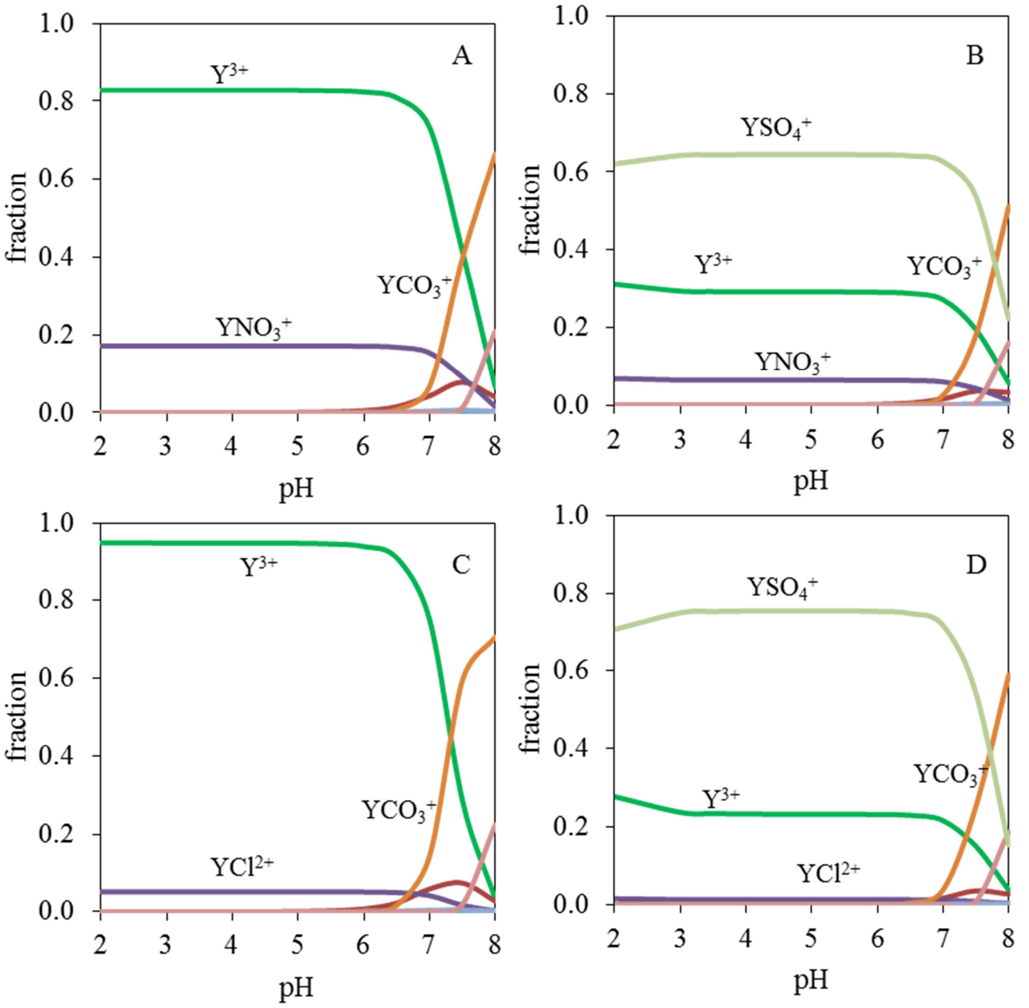


Figure S2. Atomistic representations of the three models of Y3+ adsorbed on Al-octaedral basaluminite water interface used to fit the EXAFS data of the B-YSO4-ads sample. The three models have an inner-sphere coordination with different oxygen atoms as ligands: (A) monodentate, (B) bidentate mononuclear, (C) bidentate binuclear.

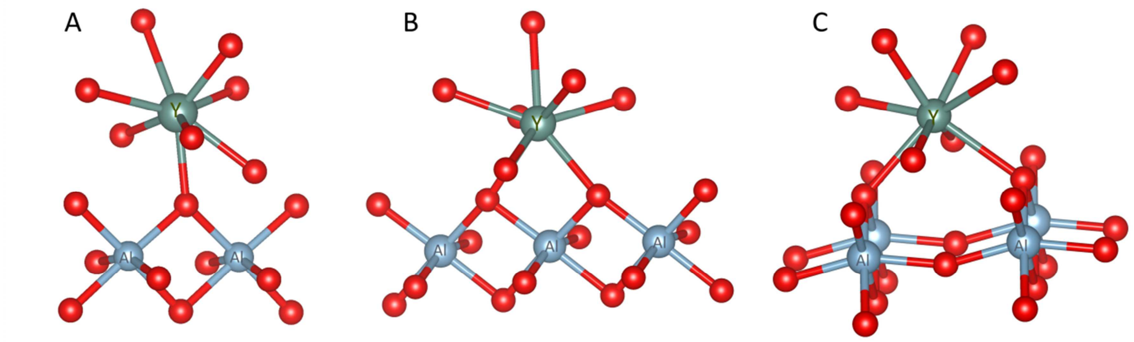


Figure S3. (A) K^3-weighted EXAFS spectra and (B) Fourier transform amplitude and real phase at Y K-edge absorbed onto B-YSO4-ads sample. Experimental and fits curves are displayed in black and red colors, respectively. Fits carried out with models represented in Fig. S2. K-range 3.41-12.20 Å^{-1}. R range 1.35-4.00 Å.

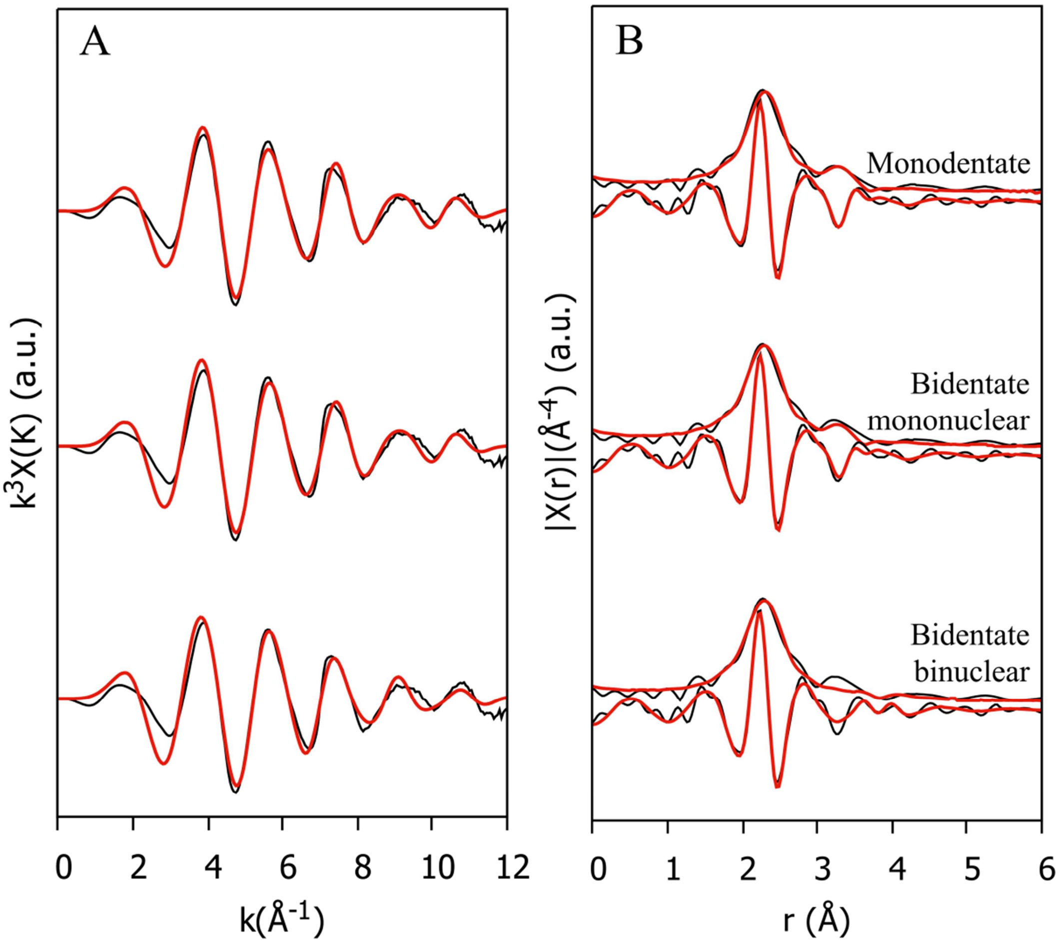


Figure S4. Experimental EXAFS spectra (solid lines) and the reconstructed spectra (red dashed lines) with 2 components (left) and with three components (right) for the four waste samples.

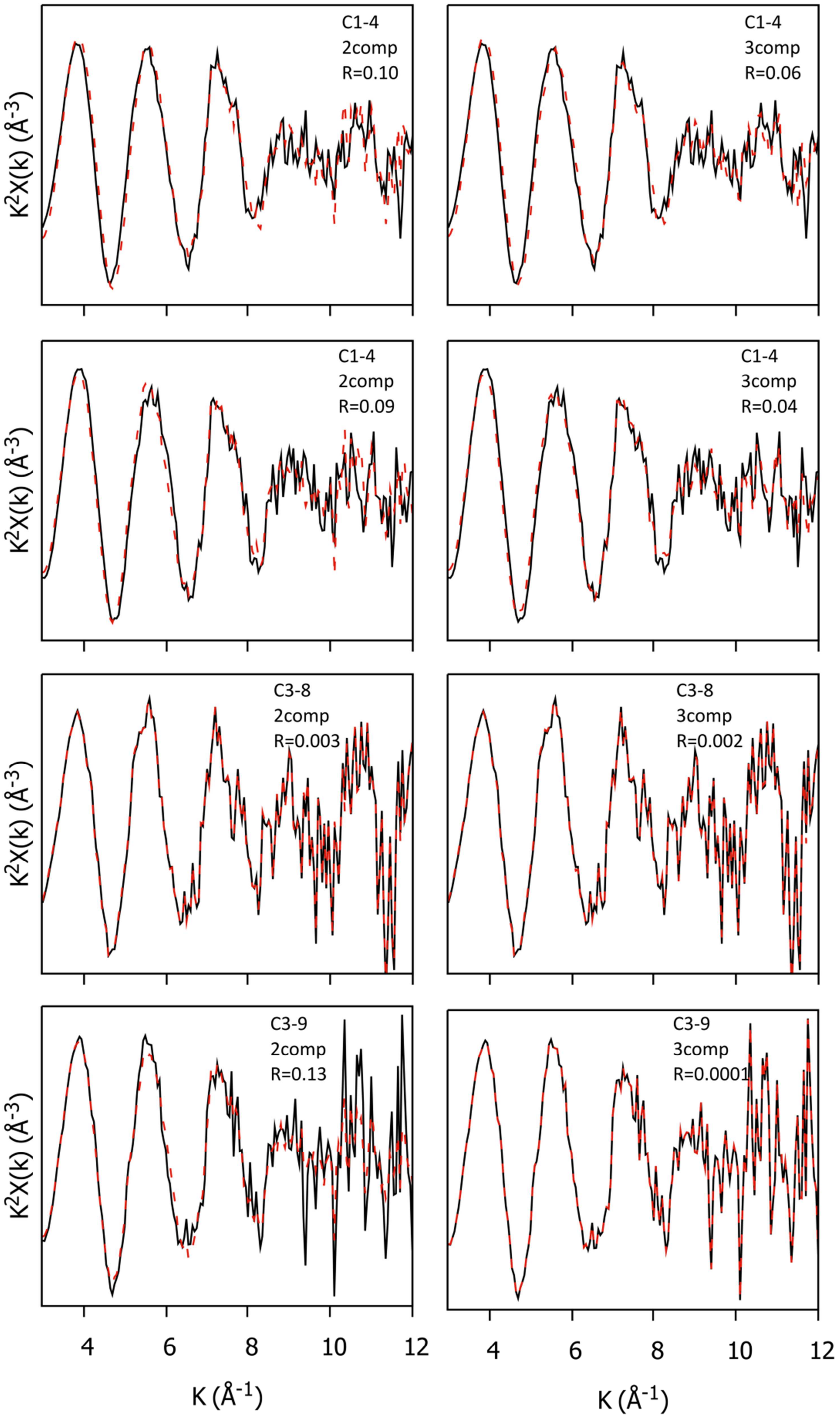
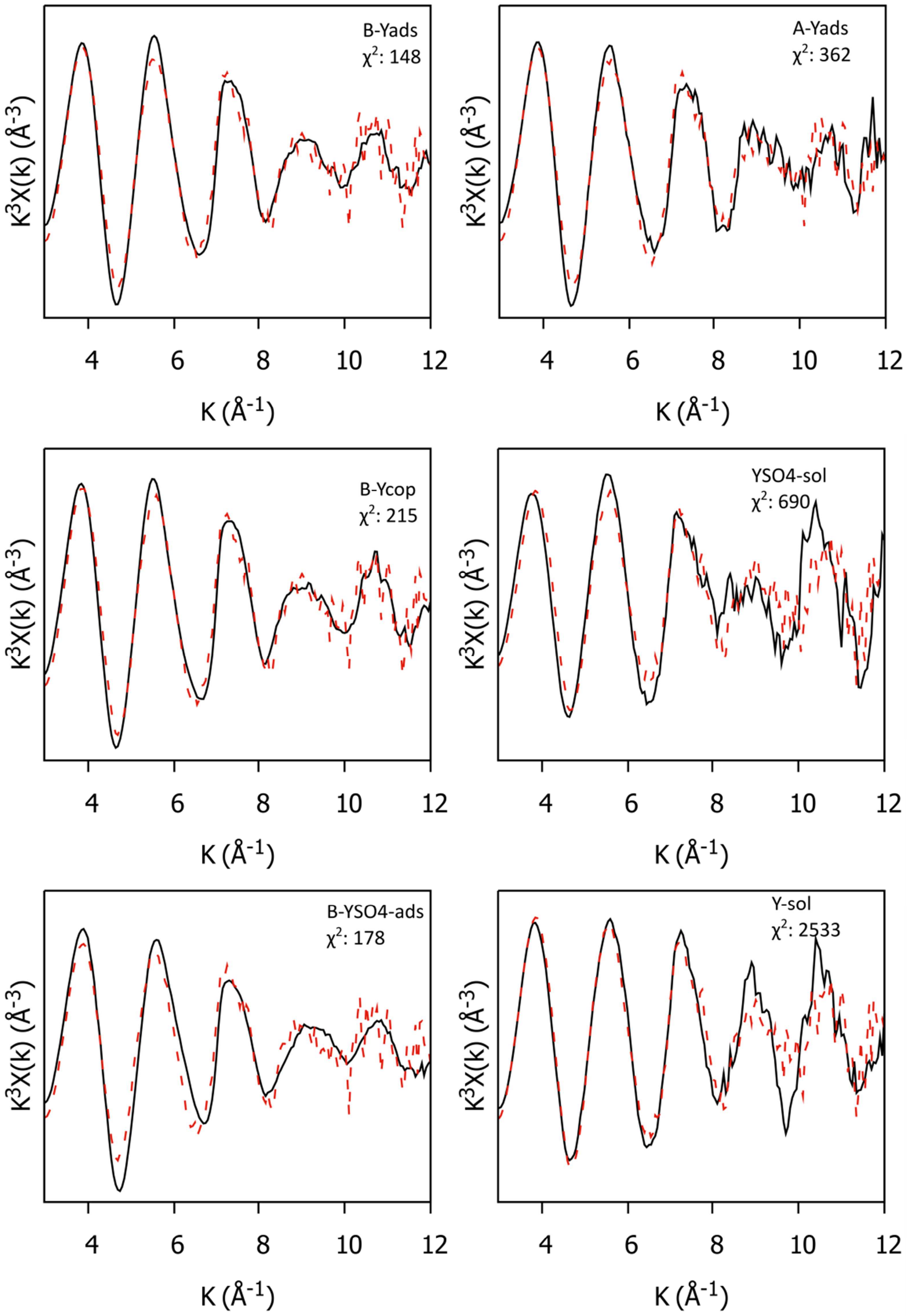


Figure S5. Target transformation (dashed lines) of waste samples EXAFS spectra (solid lines) for the six Y references. B-Yads: basaluminite with adsorbed Y^{3+}, B-Ycop: basaluminite coprecipitaetd withY^{3+}, B-YSO4-ads: basaluminite with adsorbed YSO$_4^+$, A-Yads: nanoboehmite with adsorbed yttrium;Y-sol: solution whith Y^{3+} as the main aqueous specie, YSO$_4$-sol: solution with YSO$_4^+$ as the main aqueous specie.



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Article 5

Modeling the behavior of the rare earth elements in acid drainages: achievements and limitations

To submit to: Applied Geochemistry

MODELING THE BEHAVIOR OF THE RARE EARTH ELEMENTS IN ACID DRAINAGES: ACHIEVEMENTS AND LIMITATIONS

ABSTRACT

The Rare Earth Elements (REE) are called to play a significant role in modern green technologies, but the global geographical distribution of the resource may cause supply risks to the market. On the other hand, REE concentrations in Acid Mine Drainage (AMD) are several orders of magnitude higher than the rest of surface waters and could be a future supplementary source of highly valuable REE. Moreover, due to their common use in modern industry, some toxicological studies suggest that they could have a pathogenic potential. Therefore, knowing the mobility constraints of REE in natural waters, and particularly in AMD is a target of interest.

Precipitation of schwertmannite and basaluminite occurs due to mixing of acid (and REE-rich) and neutral streams. The REE fractionation between AMD and the solid phases has been investigated in several localities from the Odiel-Tinto (SW Spain) and Arroyo del Val (N Spain) basins. The behavior of REE during the mixing is conservative at low pH (pH<3), whereas they are scavenged by the precipitates at near neutral pH. This behavior is similar to that of Al and suggests that Al-phases could be responsible for REE retention. Indeed, when Fe and Al phases can be sampled separately, schwertmannite does not contain REE, which are entirely retained in basaluminite, confirming that the las phase is the main responsible for the REE removal. According to laboratory sorption experiments, both schwertmannite and basaluminite adsorb REE at pH from 5 to 7 (4 to 6 for Sc). Therefore, the lack of REE in schwertmannite is attributed to the formation of this mineral at pH below 4, whereas basaluminite precipitation occurs at pH higher than 4.

The validity and limitations of a recently proposed thermodynamic model of REE sorption on schwertmannite and to basaluminite has been tested by comparing its predictions with the observations made. The model is able to anticipate the REE distribution pattern and confirms the selective sorption of HREE and Y with respect to LREE observed in all the samples. However, the lack of synchronism between basaluminite precipitation and the REE sorption during mixing in an open flow setting precludes an accurate prediction of the REE concentration in the solid phase.

Key words: lanthanides, yttrium, scandium, sorption, basaluminite, schwertmannite

1 INTRODUCTION

Lanthanide series (from La to Lu) plus scandium (Sc) and yttrium (Y) are referred to as Rare Earth Elements (REE) according to recommendation by the International Union of Pure and Applied Chemistry (Connellly et al., 2005). Lanthanides group can be arbitrarily divided into light (LREE: La to Nd), medium (MREE: Sm to Gd) and heavy (HREE: Tb to Lu). Due to its atomic size similarity to Ho, Y is often considered with HREE, whereas Sc has been commonly set aside the group by its small ionic radius (Chakhmouradian and Wall, 2012). The global demand of REE is in constant increase due to their role in manufacturing permanent magnets, batteries, light emitting diodes and alloys among other technological advancements. However, most of REE mineral deposits are concentrated in a few countries, where China dominates more than 90% of worldwide production (USGS, 2019). There is, therefore, a need for alternative sources of REE (Alonso et al, 2012; European Commission, 2017).

On the other hand, the Acid Mine Drainage (AMD) is one of the most widespread pollution affecting the continental waters (Nordstrom, 2011; Nordstrom et al., 2015). However, the REE concentrations in AMD are several orders of magnitude higher than the rest of surface waters and could be a future supplementary source of some highly valuable REE (Ayora et al., 2016; Steward et al.; 2017; Zhang and Honaker, 2018). Moreover, although REE have been considered of minor environmental concern, due to their common use in modern industry, some toxicological studies suggest that they could have a pathogenic potential (Zhuang et al, 1996; Dai et al., 2002; Pagano et al., 2015; Roncati et al., 2018). Therefore, knowing the mobility constraints of REE in natural waters, and particularly in AMD is a target of interest.

The mobility of REE in AMD is highly dependent on pH as observed in several field studies. Verplanck et al. (2004) examined the concentration of REE along two AMD streams with varying pH. Their results showed that REE behaved conservatively at pH values below 5 despite important Fe oxidation occurred. On the contrary, REE were scavenged from the water at higher pH. The authors discarded the precipitation of REE-bearing solids and attributed the REE removal to sorption onto Fe(III) precipitates. Similar depletion of REE constant was observed by Ferreira-da-Silva et al. (2009) when an acid discharge in the Lousal mine area (S Portugal) mixed with a tributary steam and pH increased from 3 to 6. Gammons et al. (2005a) observed a similar behavior of REE in a mountain stream affected by AMD. Samplings conducted in at three stations: upstream station (pH 3.3), intermediate (pH 5.5) and downstream (pH 6.8), showed that REE remained in solution in the two first stations. The removal at high pH was interpreted as sorption on suspended particles of undifferentiated Fe and Al hydroxides. In a similar study, Gammons et al. (2005b) collected samples along 40 km along the Patagonian Agrio river, which is initially acid due to volcanic discharges. Most of the decrease in REE load occurred immediately downstream of the confluence with a tributary that increased the pH of the Rio Agrio from 4.3 to 6.1. Due to the concomitant drop in Al concentration, these authors propose that the loss of REE is due to sorption on hydrous Al oxides.

Likewise, the REE mobility has been also assessed in AMD neutralization. There, the AMD percolation through a limestone-filled column or the direct addition of NaOH induced the successive precipitation of schwertmannite and basalumininte. Rather than in schwertmannite, the REE were preferentially allocated in the basaluminite residue (Ayora et al., 2016; Lozano et al., 2019b; Zhang and Honeker, 2018). As schwertmannite forms at pH below 4 and basaluminite at pH above 4.5, these observations are consistent with the behaviour observed in acid streams. A minor fraction of Sc was observed to be retained in schwertmannite (Zhang and Honeker, 2018; Lozano et al., 2019b).

It is well known that the process of REE transfer from water to solid phases also produces a partition among the different REE. Thus, the preferential sequestration of LREE in marine environments was attributed to the stronger aqueous complexes formed between CO_3^{2-} and HREE that maintain them in solution (Sholkovitz, 1995; Kawabe, 1999; Ohta and Kawabe, 2000). In contrast with marine environments, HREE were described to show a stronger affinity for the solid phase than the LREE in AMD systems (Verplanck et al., 2004; Gammons et al., 2005b). However, the aqueous complex with SO_4^{2-} predominates in AMD, and lanthanide sulfate stability constants do not change with increasing atomic number so that no REE fractionation would be anticipated from aqueous complexation in acidic waters (Gimeno et al., 2000). Therefore, REE fractionation if any should be intrinsic to the sorption process.

Bau (1999) studied the fractionation that results from the coprecipitation of REE and Fe oxyhydroxide (HFO) due to the neutralizing of synthetic and natural acidified solutions. He confirmed the strong pH dependence in REE retention onto HFO. This author prepared solutions where the free REE cation predominated and demonstrated that fractionation occurred regardless aqueous speciation. Thus, in the experiments performed with synthetic solutions, LREE showed less preferential attachment to the HFO than MREE and HREE, but no preferential fractionation of HREE with respect to MREE was observed. However, an increase in incorporation to the solid phase from La to Lu was observed when a natural solution was used and not only HFO but Al phases formed.

Recently, Lozano et al. (2019a) performed sorption experiments of Sc, Y and lanthanides on basaluminite. Sorption occurred at pH between 4 and 7, and increased with SO_4 concentration in the solution. The experiments also confirmed a preferential fractionation, where the affinity for the solid phase increased from La to Lu, with Y in an intermediate HREE position. These authors proposed a thermodynamic model where the formation of monodentate surface complexes of sulfate-REE aqueous species explained the measurements. Attributed to its different aqueous speciation, Sc sorbed at pH between 4 and 6 as bidentate surface complexes of both sulfate and hydroxyl-REE aqueous species. Similar sorption experiments were conducted with schwertmannite (Lozano et al., 2019b). Here, REE sorption was occurring at pH ranges similar or slightly lower than basaluminite. These authors concluded that REE were not attached to schwertmannite because this mineral formed at pH too low for REE to sorb.

The aim of the present work is to test the validity of thermodynamic models developed for REE sorption on basaluminite to predict the REE behavior in AMD environments, and discuss the main limitations and uncertainties. Precipitation of schwertmannite and basaluminite occurs due to mixing of acid (and REE-rich) and near neutral streams. Several localities of two areas, Odiel-Tinto (SW Spain) and Arroyo del Val (N Spain), with high (>2 M) and low (<0.2 M) SO_4 concentration, respectively, have been selected for sampling water and particulate. The REE fractionation in the solid phase will be predicted from the concentration in the acidic water and compared with the analytical values.

2 MATERIALS AND METHODS

2.1 Odiel river sites

The Odiel River is a 122 km long and has a catchment area of 2300 km^2, from the Aracena Mountains in the North of Huelva province to Huelva estuary in the South, a region in the Southwest of Spain. The area has an inland Mediterranean climate, with fresh winters and warm and dry summers and an average rainfall of 800 mm in mostly in winter. About one hundred of ancient mines and wastes generating AMD have been detected in the Odiel watershed (Sánchez-España et al., 2005a; Nieto et al., 2013).

The stretch of the river selected for the study has about 8 km long downstream the first mine discharge of Mina Concepción (Fig. 1). The river flow varies greatly seasonally and inter-annually. During the sampling campaign (February, 2015), the Odiel river had a flow close to 1.5 m^3/s and an alkalinity of 130 mg/L eq. $CaCO_3$ prior to enter in the mining area. In the selected section, the river receives four acid tributaries of 0.5 to 5 L/s flow and a final important discharge of 0.13 m^3/s, the Agrio river (Figure 1). From this discharge the Odiel remained acidic down to the estuarine. The evolution of the water chemistry and precipitates of the same Odiel river stretch was already described by Sanchez-España et al. (2005b).

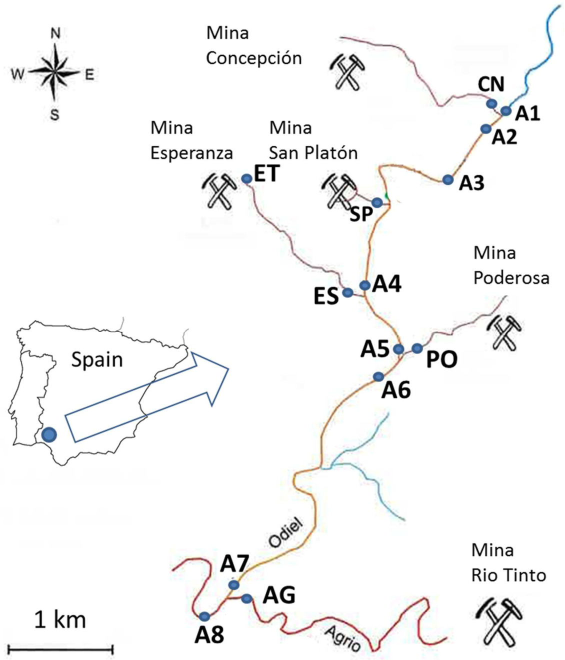

Figure 1. Stretch of the Odiel river and acidic tributaries with the sampling points.

Water samples were collected from the five water discharges (CN, SP, ES, PO and AG, Fig. 1) and from the Odiel river prior the discharges and more than 100 m downstream, when water mixing was apparently complete (Fig. 1 and Table 1). Field parameters (temperature, pH, Eh and electric conductivity) were measured at each sampling point. Water samples were filtered with 0.45 and 0.1 µm filters (Millipore), stored in 125 mL-polyethylene bottles, acidified down to pH < 2 with HNO_3, and cooled during transport. Solid samples were collected in 1 L bottles from the suspended precipitates clouds at the mixing points of acid and Odiel streams. When possible, ochre and whitish precipitates were taken separately (Fig. 2B). The water coexisting with the precipitates was labelled as PO-mix, AG-mix1 (schwertmannite) and AG-mix2 (basaluminnite). They were filtered in the laboratory the same day with 0.45 and 0.1 µm (more than one filter was needed). Filters were dried at 40°C and weighted. Then, they were digested with HNO_3 65% for 12 h at 115 °C and the solutions stored for analysis. Additional filters were also kept for mineralogical observations.

2.2 Additional sites in the Odiel-Tinto catchments

The field sampling was completed with several localities from the same area. Thus, water samples and precipitates from Dehesa Boyal (DB) and Torerera mine (TO) correspond to the mixing of a small acidic stream with less than 2 L/s (DB, TO) with a higher flow of near neutral water (DB-neu and TO-neu, repectively). The solid sample from Dehesa Boyal and Torerera remained in the bottom (Fig. 2C), and the whitish precipitates extended for more than 500 m downstream the mixing point in Dehesa Boyal (Fig. 2D). The solid samples were collected with a syringe and left to sediment in the bottle, dried and digested. The supernatant water was filtered, acidified and stored for analysis (DB-mix, TO-mix). The sampling campaigns were always carried out in February-Mars, the humid season. In summer time, the rainfall is almost absent and the rivers carry a very small flow. Due to the permanent acid discharges, the rivers become acidic and the whitish precipitates re-dissolve, whereas the reddish ones remain along the stream beds.

The Rio Tinto (RT) locality corresponds to the reverse situation. Upstream the village of Niebla, a small neutral stream of less than 5 L/s discharged into the Rio Tinto main stream (1 m^3/s). Large amounts of whitish precipitates form in the water mixing, and are carried down by the river flow until re-dissolution one hundred meters downstream (Figure 2E). Water samples were collected in the tributary (RT-neu) and the acid river (RT). Precipitates were collected in the mixing zone inside the neutral discharge where the near neutral water predominated. They were obtained from the suspended clouds in 1 L bottles, left to decant and dried. The supernatant water (RT1-mix, RT2-mix) was filtered, acidified and stored for analysis.

Finally, a full scale passive remediation system was working in 2007-8 at Mina Esperanza site (ET in Fig. 1). The system consisted in a limestone sand filter intercalated in the acid water flow. A full description of the water and solid waste chemistry and mineralogy is in Caraballo et al. (2011a,b). The basaluminite precipitates appeared during the latter three months of the treatment life, and they were probably formed by the mixing of the near-neutral outflow of the treatment with untreated acid water circulating through paths of exhausted reagent. Three solid samples of white precipitates were collected on different days at the outflow channel of treatment plant (Figure 2F). Similarly to previous cases, the precipitates were collected, left to decant and dried, and the supernatant water was filtered, digested with HNO3 and the solution stored. Unfortunately, only major solute concentrations of the water samples coexisting with the solids were available (ET1-mix, ET2-mix, ET3-mix in Table 2). No samples of the acid water were available at the moment of solid sampling. However, the chemistry of pretreated AMD was fairly constant and an averaged composition of the three later months of the treatment life compiled by Caraballo et al. (2016, Supplementary Information) was selected for modeling (ET, Table 2).The neutral outflow (ET-neu) was obtained as the average of monthly samples during the regular functioning of the treatment from April-2017 to Juny-2018.

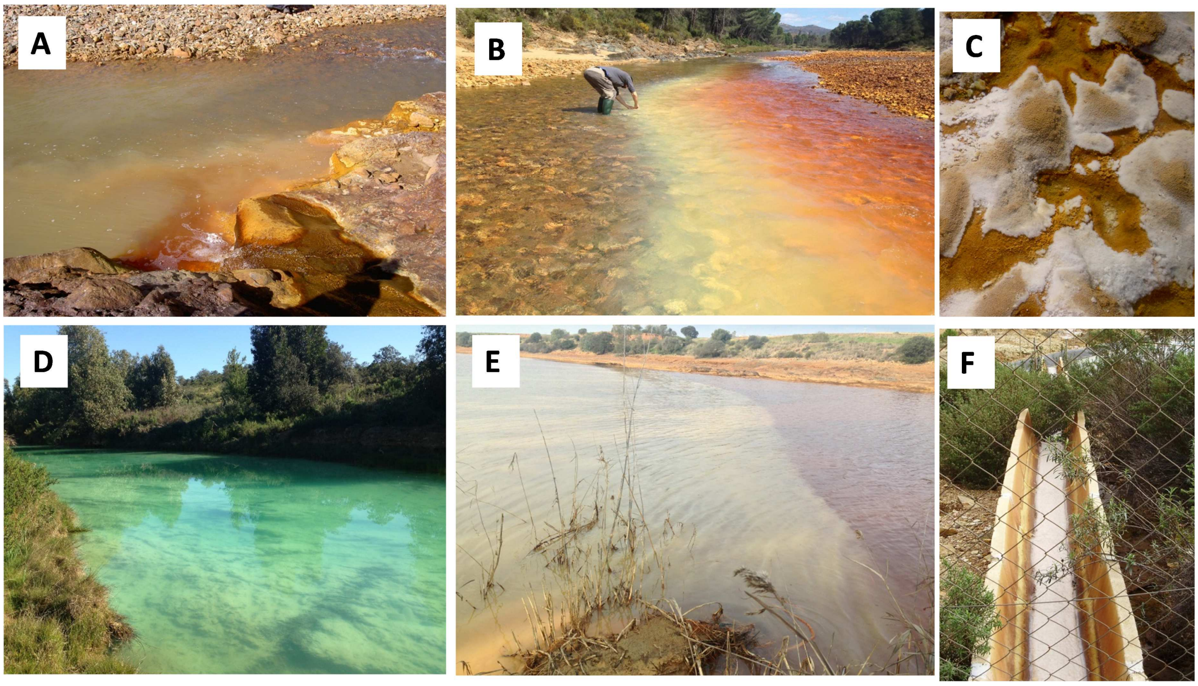

Figure 2. Pictures of the sampling points: A) precipitation of ferrhydrite (reddish) and basaluminite (whitish) at the mixing point of Mina Poderosa acid discharge and Odiel river; B) Precipitation of schwertmannite (reddish) and basaluminite (whitish)mixing point of Agrio acidic discharge (right hand of the picture) and Odiel river; C) Detail of basaluminite precipitates in Mina Torerera stream; D) Basaluminite covering the bed of Dehesa Boyal stream; E) Basaluminite precipitation at the mixing a neutral stream (left-low corner) and the Tinto river (right hand); F) Basaluminite precipitation at bottom of the outflow channel of Mina Esperanza treatment plant.

2.3 Arroyo del Val site

The information corresponding to Arroyo del Val area is mainly extracted from Auqué et al. (1993) and Gimeno (1999). The Arroyo del Val is located between Luesma and Fombuena villages, about 70 km SW Zaragoza, Spain. The area is in the Iberian Mountains, it has an inland Mediterranean climate, with cold winters and warm and dry summers and an average rainfall of 500 mm mostly in spring. The section studied of the Arroyo del Val stream is about 3 km long, it carries more than 10 L/s after rain events, and less than 1/Ls during summer. The stream is excavated in a monotonous series of dark brown to black shale of Silurian age, that crop out in the drainage basin. The black shale contain dispersed abundant sulfides, mainly pyrite, which generate a ubiquitous acid rock drainage (ARD) after weathering.

Differently from most of the Odiel sites, the Arroyo del Val is an acidic stream that receives several neutral tributaries of near neutral pH (Fig. 3). The mixing of waters yields iron and especially aluminum rich flocculates that sediment at and downstream the confluences. Water (labelled with W) and solid (labelled with C) samples were collected in three different campaigns, and only those pairs of coexisting water and precipitates were selected: 1991 (W5-CV1), 1994 (W9-C9; W12-C12) and 1996 (Wexp-Cexp). As in the Odiel-Tinto area, field parameters were measured, and the water samples successively filtered through 2, 0.45 and 0.1 µm, acidified with ultrapure HNO3 and refrigerated at 4C until analysis. Solid samples were collected from the river bed, dried and dissolved with HNO3, and the solutions stored for analysis. No samples of the supernatant water were available.

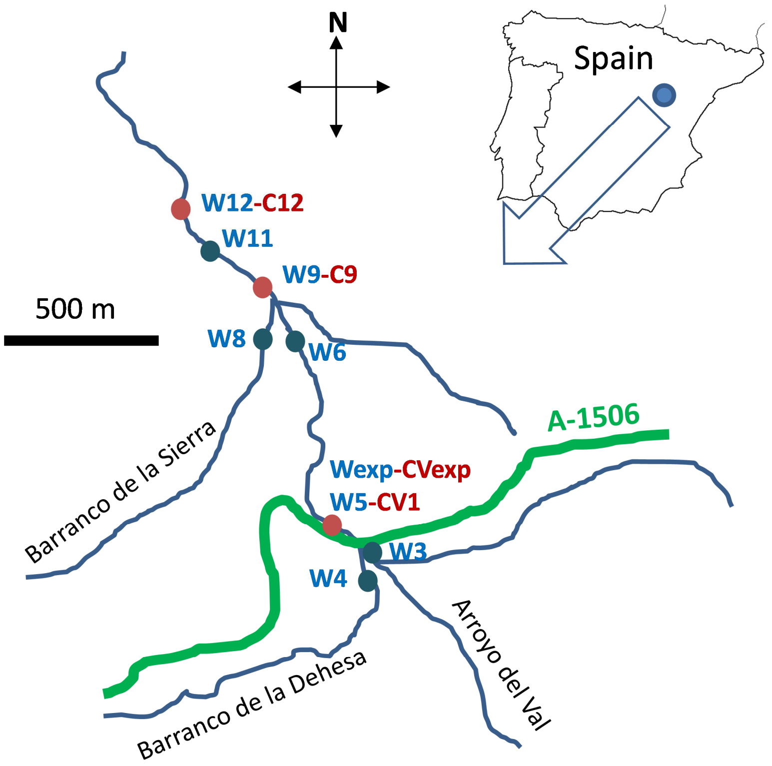

Figure 3. Sketch of the Arroyo del Val system. Each letter corresponds to different samples (W= water; C= precipitates).

2.4 Analytics

For the Odiel-Tinto sampling campaign, the field parameters such as pH, Eh, temperature (T) and EC were measured in situ with Hanna portable instruments (probetypes HI9025C, HI9033 and HI9025, respectively) properly calibrated.

Major cations (S, Al, Fe, Ca, Mg, Zn, Fe, Mn and Si) and total S were measured by ICP-AES (Perkin-Elmer® Optima 3200 RL) and trace metals (Ni, Cd, Co, Pb) and REE (La,Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y and Sc) with ICP-MS (Perkin-Elmer® SciexElan 6000). Detection limits were 0.1 mg/L for S; 0.05 mg/L for Ca, Mg, Si; 0.02 mg/L for Fe, Zn, Mn; 5 µg/L for Al; 1.5 µg/L for Cu, Ni; 0.5 µg/L for Pb; 0.1µg/L for Cd, Co and REE. Higher detection limits up to 1 µg/L resulted from dilution of in highly concentrated solutions. The analytical precision error was estimated to be approximately 7% for ICP-AES and 5% for ICP-MS measurements. Two AMD laboratory standards were also checked for REE accuracy, resulting in deviations lower than 5% of the recommended values (Verplanck et al., 2001), except for Eu which gave values 20% below the standard value.

The major mineral phases forming the solid samples were identified by X-ray diffraction (XRD) using a Bruker® D5005 X-Ray Diffractometer (XRD) with Cu Lα radiation. The samples were scanned from 0 to 60 degrees 2θ with a continuous scan at a rate of 0.025°/18 s. Granular material was also observed under a JEOL® JSM840 Field Emission Scanning Electron Microscope with Oxford Link® Energy Dispersive System (SEM-EDS).

For the Arroyo del Val site, the sampling and analytical procedures were very similar, and the details can be found in Auqué et al. (1993) and Gimeno (1999).

3 RESULTS AND DISCUSSION

3.1 REE behavior in the mixing streams

The chemical composition of the aqueous phase in each sampling point of the Odiel river stretch is listed in Table 1. These values will be compared with those resulting from the conservative mixing of the river and any acidic discharge. The theoretical concentration of any element in the river can be calculated as the addition of concentrations of the element in the acid tributary and in the river weighted with their relative flows. These relative flows are calculated from the concentration of a conservative solute in the discharge and in the river up and downstream the discharge by a simple mass balance calculation (Kimball et al., 2007). Magnesium was selected as a conservative solute since it forms very soluble salts and is practically absent in the solid phase analyses. Thus, the flow ratio between a discharge (Q_D) and the river (Q_1) was calculated as:

$$\frac{Q_D}{Q_1} = \frac{c_2 - c_1}{c_D - c_2} \tag{1}$$

where c_1 and c_2 are de Mg concentration for the river up and downstream the discharge, respectively, and c_D is the Mg concentration in the discharge.

The measured concentration of several selected solutes in the river compared with that resulting from a theoretical conservative mixing is plotted in Figure 4. Like Mg, most of divalent metals (Ni, Co, Mn, Zn, Cd) behaved conservatively and were not removed by the precipitates formed at the acid discharge-river confluences regardless the final pH of the mixture (e.g. Mn or Zn, Fig. 4A). Although some amount of SO_4 was removed from water due to Fe and Al oxy-hydrosulfate precipitates, its high concentration made it a quasi-conservative solute (Fig. 4A). On the contrary, Fe and As are clearly not conservative at both acidic and neutral pH (Fig. 4B), indicating their removal by the precipitation of schwertmannite (Carlson et al 2002; Fukushi et al., 2004). Aluminum and Cu showed an intermediate behavior (Fig. 4C). They are partially removed by precipitates in the upper part of the river, where pH remained always above 6.5, and they behaved conservatively at low pH when the Agrio acidic discharge caused a final pH of the river lower than 3.5. Similar behavior was experienced by REE. They were complete removed by the precipitates at pH higher than 6.5 and they behaved conservatively at pH below 3.5. This observation is consistent with the behavior described by previous authors (Verplank et al., 2004; Gammons et al., 2005a, b; Ferreira-da-Silva et al., 2009), and suggests that, rather than schwertmannite, basaluminite is responsible for scavenging REE from water.

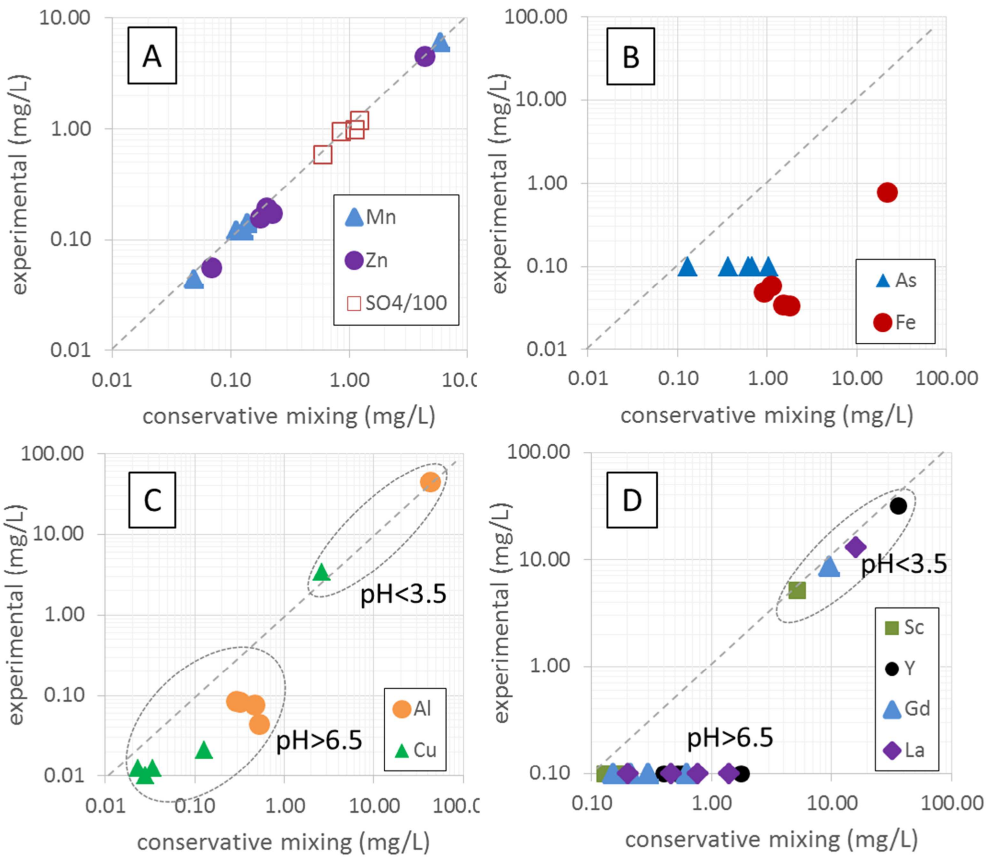

Figure 4.Comparative between experimental and conservative concentration of selected elements in samples from the Odiel river after receiving acid discharges.

The analyses of the acid waters from the rest of localities from the Odiel-Tinto area (DB, TO, RT and ET) are listed in Table 2. The Al and Fe concentration varies from 120 to 750 mg/L, and their REE concentration from 0.4 to 2 mg/L. These ranges are similar to those of the Odiel stretch described above (CN, SP, ES, PO and AG). Moreover, the filtrates coexisting with the solid precipitates sampled at the mixing zones were also analyzed for comparison (see -mix samples in Table 2). These samples were clearly different from the acid parent streams. With the exception of ET, they showed lower electric conductivity and pH values ranging from 4.5 to 6.5, and their Al, Fe and REE were always below 13, 40 and 0.07 mg/L, respectively. The ET samples showed higher EC values because the treated water also had high sulfate concentrations, and Al and Fe replaced by Ca from calcite dissolution.

The water analyses from the selected Arroyo del Val stretch are listed in Table 3. Unlike the Odiel-Tinto area, here the main flow was acidic and the tributaries supplied the alkalinity to the mixture. Another relevant difference was the sulfate concentration around 200 mg/L, lower than those from the Odiel-Tinto in more than one order of magnitude. Also electrical conductivity and the concentration of major and trace elements were significantly lower. Thus, Al and Fe concentrations were always lower than 10 and 1 mg/L, respectively, and the REE concentration was always below 0.3 mg/L.

3.2 Precipitates

Reddish-ochreous and whitish precipitates or mixtures were taken from all the localities. They are formed by aggregates of spherical particles of less than 0.1 µm forming aggregates of larger size. In most of the reddish precipitates, the pink-cushion texture typical of schwertmannite can be distinguished, whereas only aggregates of spheres were observed in the whitish precipitates.

XRD profiles show in general many peaks corresponding to quartz, illite and feldspars. This makes difficult the identification of poorly crystalline phases, unless silicates are absent of in very minor proportion. Thus, schwertmannite was only clearly identified in AG, DB and TO reddish precipitates floating in the water, and basaluminite in whitish precipitates from AG, TO, DB and ET. In the rest of localities, the existence of basaluminite was deduced from the chemical analyses.

The analyses of major and trace element concentration of all the precipitates are shown in Table 4. Reddish precipitates from AG, which were identified as schwertmannite by DRX, showed low Al content and a Fe/S ratio of 4.47 (Table 4, sample AG-r is an average of three samples), slightly lower than the range of 4.67 to 5.55 proposed for the natural variability of the mineral, $Fe_8O_8(OH)_{6-2x}(SO_4)_x \cdot nH_2O$, with x= 1 to 1.75 (Bigham et al., 1996). On the other hand, whitish precipitates from AG, DB, TO and ET showed variable but minor Fe concentrations and Al/S ratios ranging from 4.32 to 6.26, higher than the theoretical basaluminite formula, $Al_4SO_4(OH)_{10} \cdot 5H_2O$, probably due to mixtures with Al hydroxides and/or its partial transformation into low crystalline bohemite and the release of SO_4 (Lozano et al., 2018). Finally, precipitates from PO and RT show high contents in both Al and Fe, and S concentrations below 3 wt%, and (Fe+Al)/S ratios from 7.5 to 12, far above what is expected for schwertmannite and basaluminite. These samples are coincident with pH values of the mixtures above 6, and they are interpreted as mixtures of these minerals with Al and Fe hydroxides (Bigham et al., 1996; Nordstrom and Alpers, 1999). Silica was always present in basaluminite analyses with Al/Si molar ratios between 21 and 180, with the higher ratio in DB, 500 m away from the water mixing. Similar distribution of Al/Si ratios are reported by Caraballo et al. (2019).

No mineral phases other than clay minerals, K-feldspar and plagioclase were identified in the precipitates from Arroyo del Val (Auqué et al., 1993). Chemical analyses of the bulk solids were also absent, although Gimeno (1999) reported that the precipitates were formed by Al (16 to 18 wt.%), Fe (25 to 29 wt.%) and S (6 to 11%), and minor amounts of Si (1 to 6 wt.%). Moreover, microprobe analyses of the whitish amorphous phase always reveal the presence of S with ((Al+Fe)/S) ratios close to 4, which indicates that schwertmannite and basaluminite could be major phases.

More interestingly, REE were retained in basaluminite from AG in a total amount higher than 1 mg/kg when this mineral is the major phase. On the contrary, very weak or below detection level concentration was observed in the reddish precipitates of AG (AG-r). This confirms that basaluminite rather than schwertmannite was the responsible for the REE retention in the solid phase. This is consistent with the composition of the pore water from limestone columns treating AMD. There, the REE concentrations in pore water was similar or even higher than that of the inflow AMD in the schwertmannite zone, and it decreased together with Al and Cu in the basaluminite zone (Ayora et al., 2016). Similar observation was made in the neutralization with NaOH of an acid leachate from a coal coarse refuse. There, the REE were attached to the Al-rich precipitate formed at pH between 4.8 and 6.1, whereas they were absent in schwertmanite formed at lower pH (Zhang and Honaker, 2018). Therefore, the REE partition between aqueous and solid phase will be modeled here assuming sorption onto basaluminite.

3.3 Modeling REE concentration in the solid phase

3.3.1 Aqueous speciation

The activity of the aqueous species was calculated by PHREEQC code (Parkhurst and Appelo, 1999) using the Donnee Thermoddem_V1.10.dat database compiled by the Bureau de Recherches Géologiques et Minières (Blanch et al., 2012). The database has been updated with the stability constants at zero ionic strength and 25°C for the following inorganic complexes for lanthanides and yttrium: $LnCO_3^+$, $LnCO_3^{-2}$ and $LnHCO_3^{+2}$ (Luo and Byrne, 2001); $LnSO_4^+$ (Schijf and Byrne, 2004); $LnOH^{+2}$ (Klungness and Byrne, 2000), $LnOH_2^+$, $LnOH_3$ (Lee and Byrne, 1992); $LnCl^{+2}$ (Luo and Byrne, 2001); LnF^{+2}, LnF_2^+ (Luo and Millero, 2004); and $LnNO_3^{+2}$ (Millero, 1992). The Sc aqueous complexes, $Sc(OH)^{+2}$, $Sc(OH)_2^+$, $Sc(OH)_3$, $ScSO4^+$were incorporate to database. Log k values for aqueous species are compiled in Table S1 of Supplementary Information.

The presence of sulfate in solution affects REE aqueous speciation since it forms strong complexes with REE (Gimeno et al., 2000). The proportion of the REE-sulfate complex (MSO_4^+) increases with sulfate concentration and it is predominant for sulfate concentrations above 100 mg/L. Therefore, the aqueous species MSO_4^+ is the overwhelming aqueous REE species in all the acid streams and mixtures.

3.3.2 Surface complexation modeling

Lozano et al. (2019a,b) performed sorption experiments of REE onto basaluminite and schwertmannite at different pH and SO_4 concentrations. Owing to the predominance of sulfate complexes in the aqueous phase, the experiments were modelled by assuming that the aqueous MSO_4^+ complex exchanges with n protons from n surface sites XOH:

$$\mathrm{M^+ + nXOH = (XO)_nM^{1-n} + nH^+} \qquad \mathrm{K_M} \tag{1}$$

The equilibrium constant K_M of the reaction for each REE (M) would be:

$$\mathrm{K_M} = \frac{\{\mathrm{(XO)_nM^{1-n}}\}\cdot \mathrm{a_{H^+}^n}}{\mathrm{a_{M^+}}\ \{\mathrm{XOH}\}^n} \tag{2}$$

where a_{M+} and a_{H+} are the activities of the aqueous complex and proton, respectively; and $\{(XO)_nM^{1-n}\}$ and {XOH} account for the mole fraction of the sorbed species and free surface sites, respectively.

From the experimental values, Lozano et al. (2018a,b) proposed a value of n=1 (monodentate complexes) for REE sorption on basaluminite and a value of n=2 (bidentate complexes) for REE sorption in schwertmannite. Scandium speciation differed from the rest of REE, and bidentated surface complexes with $ScSO_4^+$ and $ScOH^{2+}$ were proposed for both schwertmannite and basaluminite.

The equilibrium constants of reaction 1 for basalumnite and schwertmannite are listed in Table S2, and the variation of the sorbed fraction with pH resulting from the model at 2000 mg/L SO_4 is plotted in Figure 5A and 5B, respectively. Sorption breakthrough curves for lanthanides and yttrium are similar for both minerals, although sorption in schwertmannite occurs at slightly lower pH. Sorption of Sc occurs at one unit lower pH in both minerals.

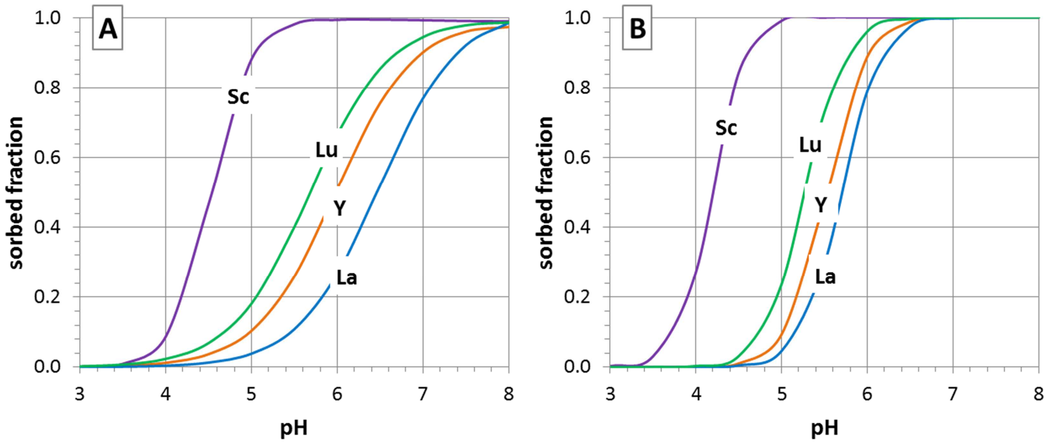

Figure 5. Variation of the fraction sorbed in basaluminite (A) and in schwertmannite (B) with pH for four selected REE, as calculated from the model described in Lozano et al (2019a,b).

3.3.3 Comparison between predicted and analyzed concentrations

According to equation 2, the REE concentration of the aqueous phase (and its aqueous speciation, a_{M^+}), and the free sorption sites (obtained from the total sorption sites) were needed to predict the REE concentration in the solid phase.

The aqueous phase coexisting with the basaluminite precipitates at the mixing points from the Odiel-Tinto localities contained very low amount of REE (samples "–mix" in Tables 1 and 2) and cannot justify the REE concentration measured in the solid phase. This is because practically all the REE content of the acidic tributaries was already transferred to the solid particles, and the "–mix" aqueous phase is mainly formed by the main flow of neutral water carrying precipitates in suspension. Therefore, the "-mix" water was not considered in equilibrium with the solid phase, and the REE concentration of the acidic stream was used as base to calculate the activity of the aqueous species in all cases. In the case of Arroyo del Val, where the acidic water was the main flow, only a minor dilution took place and the acid water upstream the mixing was used in the calculations (Table 3).

To estimate the total sorption sites we assume that all the Al transferred from the aqueous to the solid phase is converted stoichiometrically into basaluminite:

$$T_{XOH} = \frac{[Al]\cdot M_{bas}\cdot A\cdot\sigma\cdot 10^{18}}{4M_{Al}\cdot N_A} \qquad (5)$$

where T_{XOH} (mol/kgw) is the total sorption sites, [Al] is the difference of Al concentration (mg/kgw) of the acidic stream minus that of the mixture (in the Odiel-Tinto area) and minus that of the acid water downstream the mixing (in Arroyo del Val); M_{Al} and M_{bas} are the molar mass of Al and basaluminite; A is the specific surface area (m2/mg); σ are the sites obtained from the basaluminite structure (4.6 sites/nm^2 according to Lozano et al. 2019a); and N_A is the Avogadro number. The specific surface area of the precipitates was also determined and ranged from 0.030 to 0.129 m^2/mg. Since the solid phase was not pure basaluminite, the specific surface area was kept constant as 0.068 m^2/mg in all the calculations, the value of the mineral synthetized in the laboratory (Lozano et al., 2019a). The resulting T_{XOH} values are also included in Table 4.

Both, the calculated and measured REE concentration in the solid phase were normalized to the NASC standard (Gromet et al., 1984) and compared. The predicted REE concentrations were always higher than the observed. This could be due to several uncertainties, such as the estimation of the sorption sites from the drop in Al concentration, the specific surface area or the effect in the concentration by the dilution by the neutral stream and will be discussed below. In order to facilitate the comparison of the measured and calculated REE patterns, the concentrations calculated were arbitrarily multiplied by a factor f until both observed and calculated Gd values coincide (see an example in Figure 6A). Gadolinium was selected because it occupies a central location in the lanthanide series.

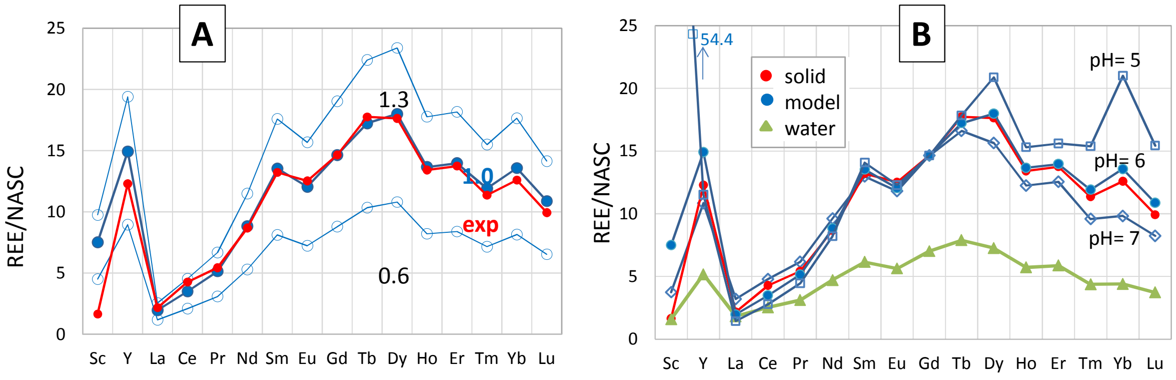

Figure 6. NASC-normalized REE distribution pattern in basaluminite calculated for three different dilution factor f (A) and pH (B) values (blue symbols). The REE pattern measured in the water (green triangles) and in basaluminite (red circles) are plotted for comparison.

A second uncertainty is the pH value at which sorption occurred. According to the sorption variation with pH calculated with the model, the different REE undergo very different sorption efficiency at a particular pH (Figure 5A). Thus at pH 5, 89, 23 and 14 % Sc, Lu and La are sorbed, respectively. At pH 7, sorption proportions are much more equilibrated, and 100, 96 and 80 % Sc, Lu and La are sorbed, respectively. The consequence of this different sorption affinity on the REE distribution pattern is relevant (Figure 6B). Thus, calculations performed at pH 5 result in Sc and HREE predicted to sorb more than LREE, and their relative values are overpredicted with respect to measurements. The reverse reasoning can be made for calculations at pH 7 (Figure 6B). This means that the REE distribution pattern is highly dependent on the sorption pH, and, inversely, the REE distribution pattern can inform about the sorption pH. The final calculated patterns were obtained by selecting manually the factor f and pH values that allow a better fit between predictions and observations.

The results are plotted in Figures 7 and 8. The REE patterns of the original acid water are also plotted as a reference. As can be observed, the main trends of REE distribution of the water are transferred to the solid phase. Thus, all the NASC-normalized REE patterns of waters and precipitates show a typical convex curvature indicating enrichment in MREE with respect to LREE and HREE, which has been also described for other acid drainages (Ferreira-da-Silva et al., 2009; Perez-Lopez et al., 2010; Sahoo et al., 2012). All the water samples from the Odiel-Tinto basins show a characteristic Eu negative anomaly, although this anomaly varies from being acute in PO, ET and AG (Figure 7) to less acute in other points of the Odiel -Tinto area. The Eu anomaly is absent in the samples from the Arroyo del Val site (Fig. 8). The reason for this different pattern seems, therefore, related to the different original rocks and mineralization types of both regions, felsic volcanics in Odiel-Tinto and sedimentary black shales in Arroyo del Val. As exception, some precipitates from Arroyo del Val show a negative anomaly in Gd that is not observed in the aqueous phase (and neither confirmed by the model). In this case, the REE/NASC plots were scaled with Eu (Fig. 8).

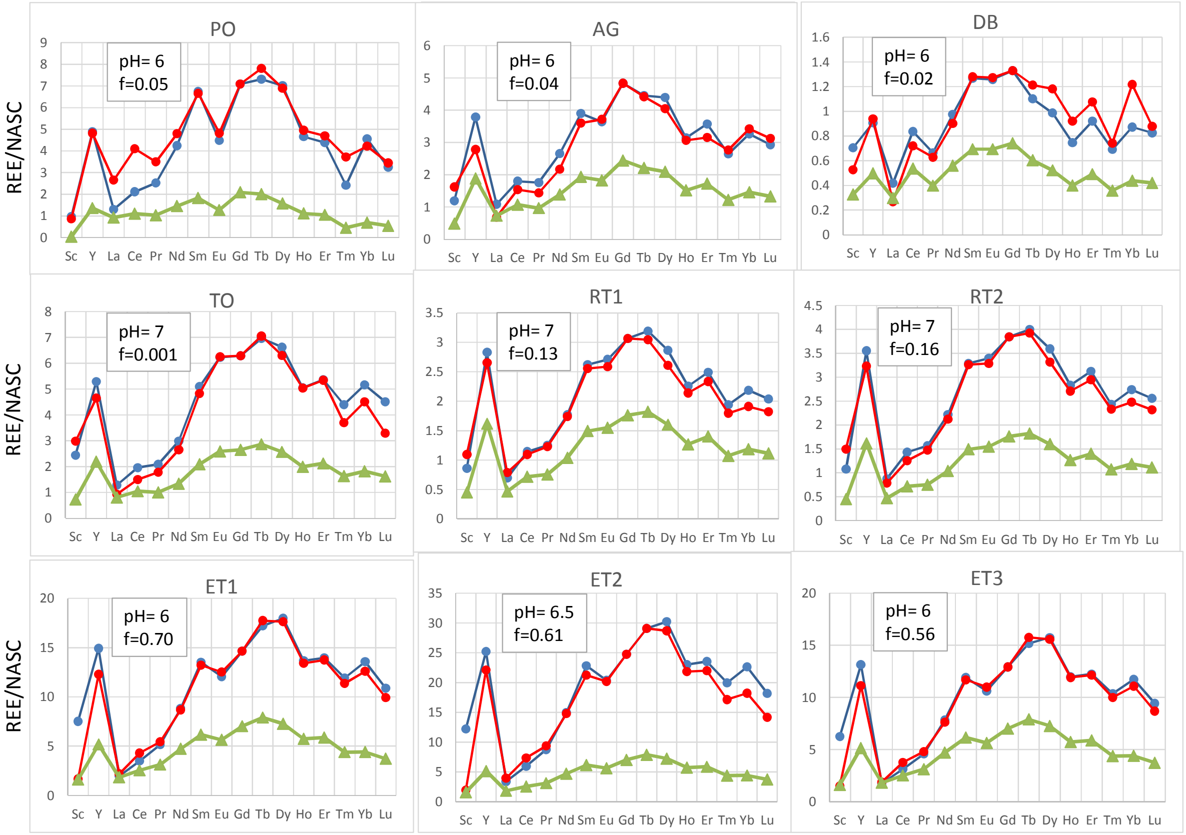

Figure 7. REE patterns of precipitates from the Odiel field area: analyzed (red) and predicted (blue). The concentrations of the parent AMD (green triangles) are also plotted for comparison. All the concentrations normalized to North American Shale Composite (NASC) and scaled to the same Gd value.

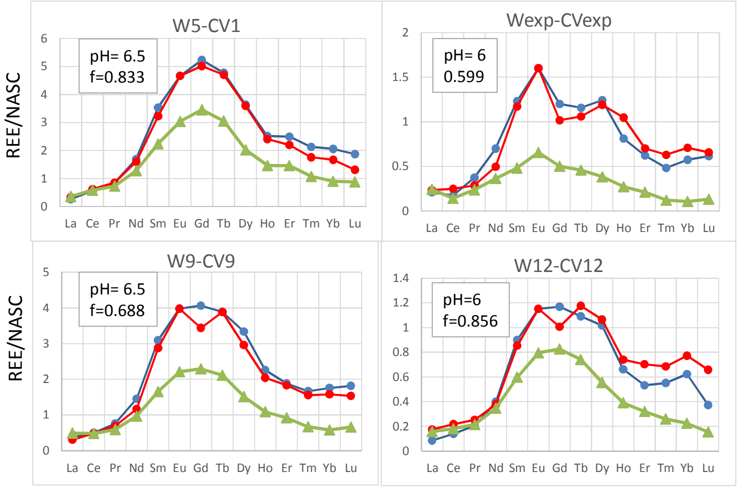

Figure 8. REE patterns of solid precipitates from the Arroyo del Vall field area: analyzed (red) and predicted (blue). The concentrations of the parent AMD (green triangles) are also plotted for comparison. All the concentrations normalized to North American Shale Composite (NASC) and scaled to the same Eu value.

The REE concentrations predicted by the model were always higher than those observed (i.e. f<1). The f value lower than 1 indicates that the sorption sites of basaluminite surface calculated from the Al removal from the liquid phase are overestimated. This overestimation could be in part due to the fact that the solid phase is not pure basaluminite, and this has been accounted by correcting the f factor with the fraction of basalumnite in the solid (calculated from its Al concentration). No Al concentration was available for the solids corrected in Arroyo del Val and no correction was made. After this correction, the final f values remained lower than 1 and are those included in Figures 7 and 8.

The dilution fraction of the acidic water in the final mixture (Q_D/Q_2 following the symbols of Eq. 1) has been calculated independently using the sulfate concentrations. Sulfate is a quasi-conservative solute far above the detection limit and gives consistent mixing proportions in the samples from all the studied localities. The dilution calculated from sulfate gives results comparable to the f factor (Figure 9). Thus, the f value is very low (f<0.05) in the cases where the acidic stream is mixed with a predominant neutral stream (PO, AG, DB, TO), and it increases to values from 0.1 to 0.2 when the mixing streams are slightly more compensated (RT). The f factor of the outflow from the treatment plant gives intermediate mixing proportions between 0.3 and 0.8, as expected for the final stages of a treatment (Caraballo et al., 2011b). Finally, the f factor is close to 1 when the acidic stream is the main flow and it is barely diluted (AV).

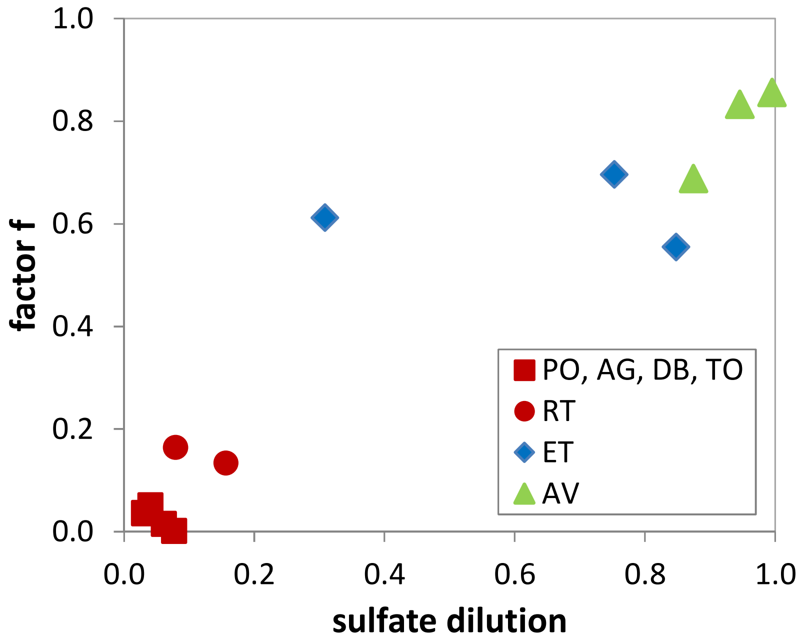

Figure 9. Dilution of AMD calculated from sulfate versus the f factor required to fit the observed and calculated REE patterns of the samples analyzed.

The consistency of the f factor with sulfate dilution suggests that dilution of the acidic water may play a major role in the REE concentration in basaluminite. However, since dilution of the acid water would also affect the Al concentration, no overestimation of the basaluminite sorption sites with respect to the REE dissolved should be expected from Eq. 5. An explanation for low f values could be that the precipitation of Al and the REE sorption are not synchronous, especially in cases with high neutral flows (such as Odiel river cases). Thus, basaluminite starts to form earlier as pH increases above 4, whereas a significant REE sorption starts at pH values between 5 and 7. In a stream flow setting, part of the flocculates could have been dispersed and did not contact with REE aqueous species at the pH value efficient for sorption. This is consistent with the high pH values of sorption deduced from the REE patterns. Thus, the best fit of the LREE and HREE patterns are generally obtained for sorption calculated at pH 6 or 7, values clearly higher than the onset of basaluminite precipitation.

It is important to note that the comparison of the patterns of AMD and solid phase (both measured and calculated) clearly show that the MREE and HREE are more favorably incorporated than LREE on the solid phase. This is consistent with laboratory sorption experiments (Fig. 5A), and with field results described in previous studies (Verplanck et al., 2004; Gammons et al., 2005b). In detail, differences between calculated and measured REE concentrations in the solid are not systematic, and a particular element is sometimes slightly over or underpredicted depending on the sample.

Owing to its much higher price than the rest of REE and that was not reported in previous studies, a special attention was devoted to Sc. According to laboratory experiments (Fig. 5B), sorption on schwertmannite occurs at pH higher than 3.5, and consistently, no Sc was detected in three samples of schwertmannite precipitates (averaged as AG-r in Table 3). This suggests that no Sc would be scavenged in the schwertamnnite precipitates frequently covering the bed of many acid streams, and it could be recovered in the treatment plants as the rest of REE (Ayora et al., 2016; Honaker et al., 2018). Nevertheless, additional sampling of water and schwertmannite precipitates in acid drainages with pH between 3 and 4 would be needed to confirm the Sc mobility.

Scandium samples from the Odiel-Tinto area showed no systematic differences between calculated and measured concentrations, with the exception of those from Mina Esperanza treatment. There, the model systematically overpredicted the Sc concentration in the outflow of the treatment system (ETs, in Fig. 7). This indicates that the Sc from the acid water was not entirely retained in the basaluminite precipitates. Indeed, as observed in a column experiment emulating an AMD treatment with limestone, part of the Sc remained adsorbed on the solid phase whereas the rest of REE were completely mobile when the acid water front progressed in the treatment (Lozano et al., 2019b). Similar preferential fractionation of Sc to the solid phase at lower pH values was observed when neutralizing a leachate from a coal waste with NaOH (Zhang and Honaker, 2018).

4 CONCLUSIONS

When an acid drainage mixes with a near neutral stream, a mixture of schwertmannite and basaluminite precipitate. The behavior of REE during the mixing is conservative at low pH (pH<3), whereas they are scavenged by the flocculates at near neutral pH. This behavior is similar to that of Al and Cu, different from Fe and As that are partially removed also at lower pH, and different from divalent metals (Zn, Mn, Cd, Co) that remain in solution at any pH. This confirms the observations made by previous studies and suggests that Al-phases could be responsible for REE retention. When Fe and Al phases can be sampled separately, schwertmannite does not contain REE, which are entirely retained in basaluminite, confirming that the las phase is the main responsible for the REE removal.

According to laboratory sorption experiments, both schwertmannite and basaluminite adsorb REE at pH from 5 to 7 (4 to 6 for Sc). Therefore, the lack of REE in schwertmannite is attributed to the formation of this mineral at pH below 4, whereas basaluminite precipitation occurs at pH higher than 4.

A non-electrostatic surface complexation model of the MSO_4^+ aqueous species (M accounting for REE except Sc), exchanging one proton with the basaluminite surface has been used to predict the REE removal in several cases of mixing acid and neutral waters. In the case of Sc, and additional species $Sc(OH)_2^+$ and the exchange two protons was required. The sorption capacity of the solid phase can be estimated from the difference between the Al initially dissolved in the acid water and the final concentration in the mixture. The model is able to anticipate the main trends of the REE distribution patterns observed in the solid phase, regardless the sulfate concentration in the acid drainage. These distribution patterns confirm the selective sorption of MREE, HREE and Y with respect to LREE.

There are, however, some uncertainties in the modeling. First, the amount of basaluminite particles (and sorption sited) that would form from the Al dissolved in the acid stream can be diluted-dispersed in the mixture. The dilution factor could be independently approximated from other conservative solutes. A second uncertainty is the estimation of the pH at which sorption occurs. This pH could be approached from the geochemical modeling of the major element chemistry and flow proportions of the two end members. All these calculations, however, assume that all the reactions occur in a close system. However, if reactions are not synchronous in an open flow setting total masses may not be conservative. Thus, basaluminite starts to form earlier as pH increases above 4, whereas the significant REE sorption occurs at pH values between 5 and 7, where some basaluminite could has been transported away. This precludes an accurate modeling of the REE concentrations of the solid phase.

Scandium adsorbs in the solid particles at pH one unit lower than the rest of REE, but it seems to behave as the rest of REE in acid streams of pH below 4. Therefore, no Sc would be scavenged in the schwertamnnite precipitates frequently covering the bed of many acid streams, and it could be recovered in the treatment plants as the rest of REE. In the treatment plants, Sc seems to be less mobile than the rest of REE.

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Tables

Table 1: Field parameters and chemical compostion of the water samples from a selected Odiel river stretch

	A1	**CN**	**A2**	**A3**	**SP**	**A4**	**ES**	**A5**	**PO**	**A6**	**A7**	**AG**	**A8**	**PO_mix**	**AG-mix1**	**AG-mix2**
Sampling date	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015	18/02/2015
UTM X	706171.3	706120.8	706089.6	705606.7	704986	704839.5	704810.2	705189.6	705203.9	705121.6	703514.9	703481.4	703294.2	705203.9	703481.4	703481.4
UTM Y	4182969.4	4182952.1	4182906.3	4182340	4182025	4181329.5	4181227.3	4180732.4	4180651.7	4180570.7	4178344	4178232.8	4178192.1	4180651.7	4178232.8	4178232.8
pH	7.69	2.87	7.58	7.51	2.7	7.56	2.89	7.53	2.34	7.41	7.53	2.75	3.9	5.2	3.4	4.87
EC (μS/cm)	229	1085	233	233	6250	242	3779	246	4816	251	253	7250	1017	380	1271	407
Eh	327	679	310	220	570	312	648	321	704	303	294	657	455	254	449	427
temperature(ºC)	12.5	10.1	12.5	12.7	18.9	13	11.6	13.3	12.9	13.4	15.1	16.3	16.5	13.1	16.6	15
Alk (mg/L CaCO3)	130		115	118		115		111		108	102					
mg/L																
Al	0.08	23.49	0.04	0.04	222.9	0.08	90.7	0.08	171.5	0.08	0.10	605.0	44.12	3.1	79.0	1.1
Ca	19.68	18.06	19.55	19.69	162.7	20.41	258.2	19.73	137.8	20.04	20.05	170.9	30.20	19.7	47.0	30.0
Cu	0.00	1.39	0.01	0.02	13.5	0.01	3.1	0.01	39.2	0.02	0.02	36.6	3.35	0.1	7.5	0.8
Fe	0.07	44.64	0.05	0.05	1406.7	0.03	473.4	0.06	651.4	0.03	0.06	310.0	0.79	3.8	14.0	0.9
K	1.40	0.50	1.10	0.69	2.3	1.79	5.4	1.33	10.2	1.47	1.21	1.1	1.53	1.3	1.2	1.3
Mg	8.85	19.18	9.05	9.43	129.7	9.57	139.7	9.66	118.7	9.91	10.01	709.8	59.81	12.6	121.0	31.0
Mn	0.01	2.03	0.04	0.10	10.9	0.12	3.5	0.12	8.1	0.14	0.14	81.6	6.02	0.3	12.0	1.8
Na	10.27	10.01	10.59	10.40	25.3	10.80	29.1	10.74	59.1	10.54	10.52	31.0	17.47	10.7	15.0	14.0
SO4	11.10	471.26	19.45	21.96	5310.2	31.42	2669.9	32.75	3516.2	39.68	43.42	7726.8	613.81	142.5	441.0	239.0
Si	4.69	12.06	4.72	4.56	55.1	4.47	32.2	4.56	51.8	4.17	4.37	30.6	6.51	4.6	7.1	3.1
Zn	0.04	1.32	0.06	0.11	91.4	0.17	2.9	0.16	20.2	0.19	0.17	59.5	4.56	1.2	16.0	2.4
μg/L																
As	<0.1	1.7	0.1	<0.1	755.0	<0.1	226.5	<0.1	119.8	<0.1	<0.1	8.3	<0.1	<0.1	<0.1	<0.1
Cd	<0.1	6.3	0.1	<0.1	260.1	<0.1	23.8	0.1	129.8	0.1	0.1	372.5	31.0	<0.1	67.5	10.5
Co	<0.1	159.8	3.7	7.1	614.2	8.0	107.5	7.8	474.9	9.1	8.8	2053.5	160.7	27.4	405.0	69.1
Ni	<0.1	13.2	<0.1	1.6	80.0	1.5	47.4	1.9	96.7	2.0	2.0	945.8	79.9	8.1	207.9	30.3
Sc	<0.1	3.7	<0.1	<0.1	24.2	<0.1	15.8	<0.1	14.3	<0.1	<0.1	72.1	5.1	3.7	16.6	<0.1
Y	<0.1	22.3	<0.1	<0.1	379.3	<0.1	133.1	<0.1	735.5	<0.1	<0.1	508.7	31.8	11.1	140.4	7.6
La	<0.1	19.1	<0.1	<0.1	546.6	<0.1	45.0	<0.1	577.0	<0.1	<0.1	226.2	12.9	4.3	62.5	3.8
Ce	<0.1	46.9	<0.1	<0.1	1416.0	<0.1	109.3	<0.1	1479.5	<0.1	<0.1	718.2	42.6	19.3	198.4	11.0
Pr	<0.1	5.5	<0.1	<0.1	174.4	<0.1	22.3	<0.1	189.5	<0.1	<0.1	88.2	5.5	2.7	24.0	<0.1
Nd	<0.1	20.7	<0.1	<0.1	661.5	<0.1	105.4	<0.1	891.0	<0.1	<0.1	423.2	23.1	5.6	113.2	6.0
Sm	<0.1	5.3	<0.1	<0.1	163.3	<0.1	26.0	<0.1	219.4	<0.1	<0.1	115.6	7.3	1.8	31.4	<0.1
Eu	<0.1	0.1	<0.1	<0.1	21.7	<0.1	5.6	<0.1	31.8	<0.1	<0.1	22.8	1.2	<0.1	6.7	<0.1
Gd	<0.1	5.9	<0.1	<0.1	160.0	<0.1	22.7	<0.1	230.2	<0.1	<0.1	134.4	8.6	3.4	36.4	<0.1
Tb	<0.1	0.1	<0.1	<0.1	21.5	<0.1	4.5	<0.1	34.2	<0.1	<0.1	18.8	1.4	<0.1	5.6	<0.1
Dy	<0.1	5.0	<0.1	<0.1	100.3	<0.1	29.0	<0.1	174.9	<0.1	<0.1	116.0	7.9	2.1	30.7	<0.1
Ho	<0.1	0.1	<0.1	<0.1	15.0	<0.1	5.1	<0.1	28.3	<0.1	<0.1	19.2	1.4	<0.1	5.8	<0.1
Er	<0.1	2.4	<0.1	<0.1	33.7	<0.1	14.0	<0.1	69.0	<0.1	<0.1	56.4	3.9	1.3	15.3	<0.1
Tm	<0.1	0.1	<0.1	<0.1	3.4	<0.1	1.6	<0.1	5.0	<0.1	<0.1	6.6	<0.1	<0.1	1.8	<0.1
Yb	<0.1	1.9	<0.1	<0.1	19.3	<0.1	9.5	<0.1	42.9	<0.1	<0.1	45.4	3.0	<0.1	12.4	<0.1
Lu	<0.1	0.1	<0.1	<0.1	2.5	<0.1	1.3	<0.1	5.0	<0.1	<0.1	6.1	<0.1	<0.1	1.1	<0.1
∑REE		139.1			3742.6		550.2		4727.3			2577.8	155.6		702.2	28.4

Table 2: Field parameters and chemical compostion of the water samples from several localities from theOdiel-Tinto rivers catchements

	DB	DB-neu	DB-mix	TO	TO-neu	TO-mix	RT	RT-neu	RT1-mix	RT2-mix	ET	ET-alc	ET1-mix	ET2-mix	ET3-mix
Sampling date	10/03/2015	10/03/2015	10/03/2015	01/02/2017	01/02/2017	01/02/2017	02/02/2017	02/02/2017	02/02/2017	02/02/2017	07 to 11/2008	2007-04/2008	29/09/2008	12/11/2008	22/10/2008
UTM X	662472.3	662366.4	665033.2	686048.1	685947.4	685977.8	710981.8	710948.8	709871.2	709871.2	704084.5	704166.2	704168.2	704166.2	704166.2
UTM Y	4156769	4156751.2	4155946.6	4162627.8	4162610.1	4162625	4143841.9	4143687.5	4142759.3	4142759.3	4181643.9	4181627.2	4181627.2	4181627.2	4181627.2
pH	2.58	6.54	4.54	2.44	6.12	5.14	2.62	6.44	5.5	5.63	2.6	6.1	4.9	4.6	5.1
EC (mS/cm)	6503	520	704	2465	261	269	1680	653	743	595	1760	1311	1403	1564	1633
Eh	629	102	369	493	216	393	397	74	240	66	397	213	283	320	301
temperature (ºC)	17.4	16.9	16.7	14.4	14.9	14.8	15.1	14	17.4	14.7	16.4	16.5			16.7
Alk (mg/L CaCO3)		130			50			225							
mg/L															
Al	742.00	0.0	6.2	350.14	0.1	3.8	136.88	0.30	12.4	10.2	149.7	0.2	22.0	18.0	5.7
Ca	123.42	39.0	33.8	200.01	15.7	17.6	50.69	100.90	95.6	96.8	181.4	692.0	482.0	522.0	643.0
Cu	78.13	0.5	1.7	9.99	0.0	0.1	25.09	0.01	2.5	1.8	24.6	0.1	11.2	12.0	3.7
Fe	490.07	0.0	0.2	128.81	0.0	1.3	503.40	0.30	40.3	34.4	1010.0	618.0	687.0	352.0	696.0
K	0.45	1.6	2.2	0.22	0.9	0.5	3.46	12.60	11.5	11.7	7.7	6.1	6.2	4.0	6.6
Mg	546.12	34.0	39.8	172.03	9.5	11.2	150.23	35.10	49.2	44.8	201.1	177.0	214.0	138.0	220.0
Mn	100.33	3.3	4.3	31.42	0.0	0.4	13.81	0.10	1.7	1.2	4.6	3.7	5.4	2.2	6.5
Na	16.22	41.0	36.5	5.60	14.7	14.2	27.54	72.30	67.9	69.1	41.23	20.60	28.0	22.0	29.0
SO4	8343.00	246.0	512.0	3681.18	39.3	283.3	2550.66	116.10	398.9	310.2	4010.1	2203.0	3563.0	2760.0	3735.0
Si	81.10	4.8	10.0	38.47	3.6	4.1	9.27	4.70	5.1	4.9	49.3	6.5	8.5	13.0	7.4
Zn	51.39	1.0	1.0	40.61	0.0	0.5	47.41	0.01	5.2	3.6	24.1	12.1	21.0	18.0	27.0
µg/L															
As	17.2	<0.1	<0.1	5.3	<0.1	<0.1	571.2	3.5	38.2	3.6	599.3	2.1			
Cd	249.8	0.6	8.2	52.0	<0.1	<0.1	142.0	<0.1	18.9	13.3	85.6	2.4			
Co	4867.0	9.5	35.2	415.1	<0.1	6.5	808.6	2.5	97.6	66.9	583.3	108.0			
Ni	2580.0	6.1	18.0	705.7	<0.1	11.2	147.9	<0.1	20.1	14.7	169.9	24.0			
Sc	97.2	<0.1	<0.1	21.9	<0.1	0.1	13.3	<0.1	0.1	0.1	23.8				
Y	268.6	<0.1	12.1	118.2	<0.1	2.0	87.3	<0.1	9.7	7.6	139.4				
La	185.4	<0.1	8.6	50.0	<0.1	<0.1	29.1	<0.1	3.4	2.7	56.9				
Ce	718.7	<0.1	25.3	139.9	<0.1	2.0	96.0	<0.1	10.5	8.6	169.6				
Pr	72.5	<0.1	2.7	18.2	<0.1	<0.1	13.7	<0.1	1.5	1.2	28.4				
Nd	340.5	<0.1	10.7	81.1	<0.1	1.2	63.1	<0.1	7.2	5.7	143.4				
Sm	82.9	<0.1	2.5	25.1	<0.1	<0.1	17.9	<0.1	2.0	1.6	36.8				
Eu	17.3	<0.1	<0.1	6.5	<0.1	<0.1	3.9	<0.1	<0.1	<0.1	7.0				
Gd	81.5	<0.1	3.0	29.2	<0.1	<0.1	19.4	<0.1	2.2	1.8	38.6				
Tb	10.3	<0.1	<0.1	4.9	<0.1	<0.1	3.1	<0.1	<0.1	<0.1	6.7				
Dy	57.9	<0.1	2.3	28.5	<0.1	<0.1	17.7	<0.1	2.0	1.7	40.3				
Ho	10.1	<0.1	<0.1	5.1	<0.1	<0.1	3.2	<0.1	<0.1	<0.1	7.3				
Er	32.2	<0.1	1.3	13.9	<0.1	<0.1	9.2	<0.1	1.1	<0.1	19.2				
Tm	3.9	<0.1	<0.1	1.8	<0.1	<0.1	1.2	<0.1	<0.1	<0.1	2.4				
Yb	27.2	<0.1	<0.1	11.3	<0.1	<0.1	7.4	<0.1	<0.1	<0.1	13.7				
Lu	3.8	<0.1	<0.1	1.5	<0.1	<0.1	1.0	<0.1	<0.1	<0.1	1.7				
∑REE	2010.0			556.9			386.2				735.2				

Table 3: Field parameters and chemical compostion of the water samples from Arroyo del Val stream

	W-3	W-4	W-5	W-exp	W-6	W-8	W-9	W-11	W-12
Sampling date	1991	1991	1991	1996	1991	1991	1991	1991	1991
UTM X	654396.9		654345.6	654345.6	654190.8		654148.2	654055.6	653948.2
UTM Y	4556733.7		4556767.8	4556767.8	4557216.5		4557281.9	4557370.1	4557467.1
pH	3.32	7.45	4.55		3.90	7.02	4.58	4.39	4.72
EC (mS/cm)	539.00	570	465.00		518.00	315	453.00	449.00	428.00
Eh	839.00	322	672.00		731.00	498	614.00	721.00	685.00
temp ©	21.50	21.80	21.30		22.90	21.00	22.40	22.20	22.00
Alk (mg/L CaCO3)							11.59		
mg/L									
Al	8.30	0.20	3.80		4.10	0.20	0.40	2.70	1.50
Ca	17.90	33.20	30.80		26.00	26.70	30.01	30.10	32.20
Cu	0.02	0.01	0.02		0.02	0.01	0.01	0.02	0.02
Fe	0.05	0.12	0.26		0.31	0.11	0.17	0.23	0.28
K	2.10	1.40	1.90		1.70	1.10	1.60	1.60	1.70
Mg	23.50	18.50	25.80		24.20	15.80	24.70	27.20	27.80
Mn	1.42	0.02	0.84		0.98	0.04	0.56	0.96	0.91
Na	10.00	10.00	10.00		10.10	8.00	9.00	11.00	11.00
SO4	221.00	72.00	209.00		199.00	69.00	174.00	209.00	208.00
Si	58.54	11.60	17.69		43.97	9.00	9.85	38.76	12.20
Zn	1.26	0.05	0.80		0.62	0.05	0.44	0.70	0.75
mg/L									
Sc									
Y	46.00		26.00		29.00		13.00	24.00	19.00
La	11.90		5.60	25.00	8.40		5.10	7.40	7.00
Ce	34.50		19.50	31.70	0.20		10.80	20.90	17.20
Pr	6.00		3.30	7.20	3.80		1.80	3.40	2.80
Nd	35.90		19.50	36.80	21.40		9.80	18.80	15.10
Sm	11.70		6.70	9.60	7.80		3.30	6.70	5.10
Eu	3.40		1.90	2.73	2.20		0.92	1.90	1.42
Gd	17.40		9.50	9.20	9.80		4.20	8.30	6.50
Tb	2.20		1.30	1.30	1.50		0.60	1.20	0.90
Dy	10.10		5.60	7.10	6.90		2.80	5.80	4.40
Ho	1.67		0.93	1.15	1.10		0.46	0.90	0.71
Er	3.90		2.40	2.30	2.50		1.00	2.00	1.50
Tm	0.48		0.29	0.22	0.30		0.12	0.30	0.20
Yb	2.40		1.40	1.10	1.60		0.60	1.30	1.00
Lu	0.30		0.20	0.20	2.30		<0.1	0.20	0.10
∑REE	187.85		104.12	135.60	98.80		54.50	103.10	82.93

Table 4: Chemical composition of the precipitates sampled from the Odiel-Tinto and Arroyo del Val area. SS accounts for basaluminite sorption sites.

	PO	AG	AG-r	DB	TO	RT	RT2	ET1	ET2	ET3	CV1	C5A	Cexp	C9	C12
wt %															
Al	13.65	27.52	1.24	20.94	25.76	11.45	14.05	27.48	27.63	28.28					
Fe	16.26	8.29	45.06	1.79	4.46	23.03	25.88	4.06	5.24	0.53					
S	3.41	5.49	5.77	4.56	7.51	2.24	2.66	7.53	7.27	6.81					
Si	0.670	1.330	0.010	0.120	1.100	0.170	0.170	0.621	0.652	0.814					
Al/S (molar)	4.75	5.94	0.26	5.44	4.07	6.06	6.26	4.32	4.51	4.92					
Fe/S (molar)	2.73	0.87	4.47	0.22	0.34	5.89	5.58	0.31	0.41	0.04					
(Al+Fe)/S	7.48	6.81	4.73	5.66	4.41	11.95	11.84	4.63	4.92	4.97					
Al/Si	21.12	21.46		180.93	24.29	69.85	85.71	45.88	43.95	36.02					
mg/kg															
Sc	12.9	24.2	<0.4	7.9	44.5	16.3	22.3	24.7	29.1	22.5					
Y	130.2	75.1	3.6	25.4	125.7	71.7	87.3	331.6	597.3	300.7					
La	82.7	21.3	8.0	8.3	28.8	24.5	24.4	67.7	123.7	58.6	10.40	5.98	7.30	9.60	5.40
Ce	274.8	103.1	17.9	48.2	100.7	73.4	84.1	286.9	493.3	252.8	41.50	22.50	16.60	32.30	14.60
Pr	31.9	13.1	2.1	5.7	16.2	11.2	13.4	49.4	85.5	43.8	7.70	4.20	2.60	6.30	2.30
Nd	145.9	66.0	9.2	27.4	80.7	52.9	64.4	263.8	449.7	231.9	48.60	23.50	15.10	35.50	11.50
Sm	39.8	21.5	1.8	7.7	28.9	15.3	19.5	79.0	127.1	70.0	19.30	11.50	7.00	17.20	5.10
Eu	6.0	4.6	<0.4	1.8	7.8	3.2	4.1	15.6	25.2	13.7	5.83	3.07	2.00	4.97	1.44
Gd	39.0	26.6	1.5	7.3	34.6	16.9	21.1	80.5	136.1	71.1	27.60	11.80	5.60	18.90	5.54
Tb	6.6	3.8	<0.4	1.2	6.0	2.6	3.3	15.1	24.7	13.4	4.00	2.00	0.90	3.30	1.00
Dy	38.2	22.4	1.0	7.1	34.9	14.4	18.4	97.6	159.0	86.3	19.90	10.30	6.60	16.40	5.90
Ho	6.3	3.9	<0.4	1.3	6.4	2.7	3.4	17.0	27.8	15.1	3.06	1.54	1.33	2.59	0.94
Er	15.4	10.3	<0.4	3.5	17.5	7.6	9.6	45.0	72.0	39.7	7.20	3.80	2.30	6.00	2.30
Tm	2.0	1.5	<0.4	<0.4	2.0	1.0	1.3	6.1	9.3	5.4	0.95	0.55	0.34	0.84	0.37
Yb	13.1	10.7	<0.4	3.8	14.0	5.9	7.7	39.1	56.6	34.5	5.20	3.30	2.20	4.90	2.40
Lu	1.6	1.4	<0.4	<0.4	1.5	0.8	1.1	4.5	6.5	4.0	0.60	0.40	0.30	0.70	0.30
SS (mol/kgw)	5.5E-04	2.0E-03		2.4E-03	1.1E-03	4.1E-04	3.9E-04	3.6E-04	3.9E-04	4.0E-04	1.5E-05	1.5E-05	1.5E-05	1.2E-05	3.9E-06

Annex

Table S1. Aqueous speciation constants for Sc, Y and lanthanides (M) with different ligands (L). References: [a]: Klugness & Byrne, 2000 ; [b]: Lee & Byrne, 92;

c: Luo & Byrne, 2004;d: Millero, 92; e: Luo & Millero, 2004; f: Schijf & Byrne, 2004; g: Luo & Byrne,2001; h: Wood and Samson, 2006 (for Sc speciation).

Reaction	**log $_L\beta_n$**	**Sc**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Ref**
$M^{+3} + H_2O = M(OH)^{+2} + H^+$	log $_{OH}\beta^*_1$	-4.31	-7.8	-8.81	-8.34	-8.32	-8.18	-7.84	-7.76	-7.83	-7.64	-7.59	-7.56	-7.52	-7.39	-7.45	-7.27	a
$M^{+3} + 2H_2O = M(OH)_2^+ + 2H^+$	log $_{OH}\beta^*_2$	-9.7	-16.4	-18.14	-17.6	-17.27	-17.04	-16.51	-16.37	-16.37	-16.18	-16.1	-16.07	-15.96	-15.88	-15.74	-15.67	b, h
$M^{+3} + 3H_2O = M(OH)_3 + 3H^+$	log $_{OH}\beta^*_3$	-16.1	-25.99	-27.9	-27.23	-26.63	-26.4	-25.91	-25.41	-25.28	-25.08	-24.83	-24.56	-24.35	-24.18	-23.85	-23.85	b, h
$M^{+3} + CO_3^{-2} = MCO_3^+$	log $_{CO3}\beta_1$	-	7.48	6.73	7.06	7.23	7.28	7.46	7.48	7.39	7.46	7.56	7.55	7.61	7.68	7.81	7.75	c
$M^{+3} + HCO_3^- = MHCO_3^{+3}$	log $_{HCO3}\beta_1$	-	2.32	2.34	2.31	2.25	2.28	2.34	2.47	2.36	2.46	2.5	2.46	2.49	2.52	2.53	2.49	c
$M^{+3} + 2CO_3^{-2} = M(CO3)_2^-$	log $_{CO3}\beta_2$	-	12.63	11.3	11.76	12.08	12.17	12.53	12.63	12.48	12.78	12.91	13	13.12	13.27	13.3	13.37	c
$Ln^{+3} + NO_3^- = LnNO_3^{+2}$	log $_{NO3}\beta_1$	-	-	0.58	0.69	0.69	0.79	0.78	0.83	0.47	0.51	0.15	0.25	0.15	0.2	0.25	0.56	d
$M^{+3} + F^- = MF^{+2}$	log $_F\beta_1$	-	3.97	3.11	3.29	3.35	3.29	3.61	3.72	3.71	3.83	3.88	3.78	3.77	3.77	3.84	3.74	e
$M^{+3} + 2F^- = MF_2^+$	log $_F\beta_2$	-	6.35	5.16	5.48	5.66	5.66	5.99	6.11	6.07	6.24	6.29	5.98	5.96	6.09	6.31	6.31	e
$Ln^{+3} + SO_4^{-2} = LnSO_4^+$	log $_{SO4}\beta_1$	4.18	3.5	3.61	3.61	3.62	3.6	3.63	3.64	3.61	3.59	3.57	3.54	3.51	3.48	3.46	3.44	f,h
$M^{+3} + Cl^- = MCl^{+2}$	log $_{Cl}\beta_1$	-	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	g

Table S2. Equilibrium contants for the REE surface complexation reac
onto basaluminite and schwertmannite (from Lozano et al., 2019a,b)

	Basaluminite		Schwertmannite	
Element	Surface Complex	Log K	Surface Complex	Log K
Sc	$(XO)_2ScSO_4^-$	-5.19	$(XO)_2ScSO_4^-$	-5.27
	$XOSc(OH)_2$	-5.81	$(XO)_2ScOH$	-3.4
Y	$XOYSO_4$	-2.48	$(XO)_2YSO4^-$	-7.62
La	$XOLaSO_4$	-2.95	$(XO)_2LaSO4^-$	-7.96
Ce	$XOCeSO_4$	-2.81	$(XO)_2CeSO4^-$	-7.6
Pr	$XOPrSO_4$	-2.69	$(XO)_2PrSO4^-$	-7.52
Nd	$XONdSO_4$	-2.60	$(XO)_2NdSO4^-$	-7.44
Sm	$XOSmSO_4$	-2.48	$(XO)_2SmSO4^-$	-7.27
Eu	$XOEuSO_4$	-2.50	$(XO)_2EuSO4^-$	-7.41
Gd	$XOGdSO_4$	-2.50	$(XO)_2GdSO4^-$	-7.51
Tb	$XOTbSO_4$	-2.48	$(XO)_2TbSO4^-$	-7.42
Dy	$XODySO_4$	-2.37	$(XO)_2DySO4^-$	-7.27
Ho	$XOHoSO_4$	-2.40	$(XO)_2HoSO4^-$	-7.38
Er	$XOErSO_4$	-2.40	$(XO)_2ErSO4^-$	-7.39
Tm	$XOTmSO_4$	-2.27	$(XO)_2TmSO4^-$	-7.17
Yb	$XOYbSO_4$	-2.13	$(XO)_2YbSO4^-$	-7.26
Lu	$XOLuSO_4$	-2.19	$(XO)_2LuSO4^-$	-7.13