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

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ABSTRACT

Yttrium belongs to the rare earth elements (REE) together with lanthanides and scandium. REE 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 is moderately enriched in REE. In fact, in passive remediation systems, which are implemented to minimize the environmental impacts of AMD, REE are mainly retained in basaluminite, an aluminum hydroxysulfate precipitate. In this study, the solid and liquid speciation and the local structure of yttrium were 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 at the aluminum hydroxide surface. EXAFS of the column samples show that its signal is represented in more than 75% by the signal of a basaluminite which YSO_4^+ is forming an inner-sphere complex. The atomic vision of the REE configuration in AMD environments could help for a deeper research of the REE recovery from waste generated in the AMD remediation systems.

INTRODUCTION

Yttrium belongs to Rare Earth Elements (REE) group, also composed by lanthanides and scandium. REE are necessary for the development of modern technologies, and specifically, yttrium as important applications, for instance, in fluorescent lamps as phosphors,¹ and in aircraft industry, used in the thermal barrier coatings for jet engines.² The REE increasing demand but low worldwide supply has led to consider REE 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. The 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 AMD (SW Spain).^{12,13} The REE 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 REE in the two treated AMD. Basaluminite, an aluminum oxy-hydroxysulfate ($\text{Al}_4(\text{SO}_4)(\text{OH})_{10}\cdot 5\text{H}_2\text{O}$), precipitates in acidic environments as a consequence of the natural attenuation of the AMD when mixing 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 the presence of 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 with a decrease in REE concentration from AMD when mixed with natural water.¹⁶ Recently, the scavenge of REE 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 REE to form aqueous species with sulfate is very high, the MSO_4^+ aqueous complex being the more abundant in AMD solutions.¹⁸ Sorption of dissolved REE 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 REE 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 REE (M). Thus, the MSO_4^+ aqueous complex is the major REE species in solution and explains that the sorption models of REE 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 REE (LREE La to Pm) to CN ~ 8 oxygen atoms for heavy REE (HREE Tb to Lu), with intermediate values for medium REE (MREE 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 that 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 REE with different ligands. REE easily forms inner-sphere complexes with carbonate and phosphate in solution³¹⁻³³ whereas chloride and nitrate forms 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. Due to its chemical similarities with HREE, this allow us to assume similar structural configuration for this sub-group. 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, (3) a bidentate binuclear inner sphere complex.

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

MATERIAL AND METHODS

Synthetic samples (standards)

Different basaluminites doped with Y were prepared for 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-YSO4-ads) was obtained from a suspension of 1g/L of solid in 0.11 $Y(NO_3)_3 \cdot 6H_2O$ and 0.25 M Na_2SO_4 solution for 5 hours at a constant pH of 6. At these conditions, the major species in solution was YSO_4^+ , which is supposedly the aqueous Y specie 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 $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (see Chapter S1 of the SI). Basaluminate 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 $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution for 5 hours, and the pH was maintained at ~ 6 at room temperature, respectively (the synthesis protocol is described in detail in Chapter S1 of the SI). At these conditions, the major species of Y is Y^{3+} . In all cases, the suspensions were centrifuged at 4500 rpm for 15 minutes, the supernatant was filtered through 0.2 μm membranes and kept for ICP analysis. The solids were rinsed several times with deionized water and oven dried for 48 hours 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 $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at pH 3.2, and a solution containing YSO_4^+ as the major aqueous complex (YSO₄-sol) were prepared by mixing equal amounts of 0.2 M $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 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 $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ at pH 4.6, and the solution of the YSO_4^+ complex (YSO₄-sol) with a composition of 0.01 M $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.01 M Na_2SO_4 at pH 2.9, were prepared, respectively. At these conditions, the major species in solution were Y^{3+} and YSO_4^+ (Fig. 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 AMD from the Iberian Pyrite Belt region (SW Spain). The columns (9.6 cm inner diameter and 39 cm in height) consisted in a permeable mixture of grained limestone and wood shavings at a 1:1 weighed ratio. Samples W-MR-C1-4 and W-MR-C1-5 belonged to columns which treated AMD from Monte Romero mine and 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 3.5 and 11.7 mg/L. Physical-chemical parameters and water samples were collected every two weeks. Once the treatment finished after 18 weeks, the solid was divided in 2 cm thick slices and dried. The partitioning of Al, Fe and REE was studied by performing a sequential extraction adapted from Torres and Auleda to the solid residues.³⁵ The results showed in Ayora et al. concluded that REE 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 most enriched in basaluminite solid slice. 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 optical emission spectroscopy (ICP-OES), 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 code³⁶ using the Donnee Thermoddem_V1.10 database³⁷ 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 PDF for aqueous solutions were obtained by subtracting the scattering signal of pure water from the total scattering signal of YSO₄-sol sample and Y-sol sample, respectively. The differential pair distribution functions (d-PDF) for B-Ycop sample were obtained by subtracting the PDF signal of a pure synthetic basaluminite from the PDF of B-Ycop sample.

The EXAFS measurements of the samples B-Yads, B-Ycop, A-Yads, Y-sol and YSO₄-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-YSO₄ sample was performed at the Y K-edge (17.038 keV) at CLÆSS beamline (ALBA synchrotron). Atomistic models of YSO₄⁺ and Y³⁺ 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 $\text{Y}^{3+}\text{-SO}_4^{2-}\text{-OH}^-$ 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 S4.

RESULTS AND DISCUSSION

Geometry of the aqueous complex YSO_4^+

The experimental (YSO4-sol, Y-sol) and theoretical (YSO4-calc) PDFs of the Y-containing aqueous solutions, 0.1 M YNO_3 and YSO_4 , are shown in Fig. 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 YSO4-sol sample shows a small and sharp peak at 1.45 Å that corresponds unequivocally to the S-O interatomic distance in sulfate, and another

smaller peak at ~ 3.6 Å, which is absent in 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.

Figure 1. (A) Top: Experimental PDFs of YSO4-sol and Y-sol samples. Bottom: Simulated (AIMD) PDF (YSO4-calc) and partial PDFs of an YSO_4^+ aqueous complex. (B) Fourier-filtered signal from 1.8 to 4.2 Å for the EXAFS data. (C) EXAFS FT amplitude functions of the YSO4-sol sample. Black lines: experimental; red lines: fits. Simulated (AIMD) PDF and partial PDFs have been multiplied for visualization purposes: YSO4-cal ($\times 3$), Y-S ($\times 5$) and Y-O and S-O ($\times 2$). Dashed lines indicate the position of the Y-O, Y-S and S-O bonds in YSO4-sol sample.

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 YSO₄-sol (Table 1). The intense peak in the FT function at 2.38 Å for the two aqueous references represents the first solvation shell, and its asymmetry reveals a distribution of Y-O interatomic distances, as reported previously by Lindqvist et al.²⁴ The coordination numbers (CN) were 7.6 ± 1.9 and 7.9 ± 0.9 for Y-sol and YSO₄-sol, respectively, which are close to the expected value of 8 for HREE. A second shell is visible in the FT of the YSO₄-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 YSO₄⁺ aqueous species forms a monodentate inner-sphere complex.

Table 1. Modeling parameters of the Y K-edge EXAFS spectra of the 0.1 M YSO₄ aqueous solution (the error is expressed in the parentheses after the last digit).

Sample	Neighbor	path	N	σ^2	ΔE_0	R (Å)	Var.	χ^2_v
Y sol	1 st shell	Y-O	7(2)	0.005(3)	-2(3)	2.37(2)	4	354
Y-SO ₄ sol	1 st shell	Y-O ₁	7.9(9)	0.007(2)		2.38(1)	8	498
	2 nd shell	Y-S	1 _{fixed}	0.003(6)	-1(1)	3.50(4)		
	3 rd shell	Y-S-O	1 _{fixed}	0.015(19)		3.18(10)		

The determined Y-O first shell coordination numbers and interatomic distances are consistent with previous reports describing yttrium coordination shells with $N = 8$ and Y-O distances of $2.36 \text{ \AA}$.^{23,24,28} Likewise aqueous REE carbonate and phosphate complexes,³¹⁻³³ aqueous Y-SO₄ ion-pairs form inner-sphere complexes. This result contrasts with other ligands such as chloride, which hardly forms inner sphere complexes at similar concentrations to those used in this study.²³ Only the formation of monodentate complexation between Dy and NO₃ with a distance of $3.57 \text{ \AA}$ has been reported using MD simulations.²⁶

Local order of yttrium adsorbed into 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 Fig. 2 with the differential PDF obtained by subtracting the pure sample from the coprecipitated one. This approach has been previously used to examine the local order of different anions incorporated in 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 $\sim 1.46 \text{ \AA}$, Al-O bonds at $1.88, 4, 4.8$ and $6 \text{ \AA}$ and Al-Al bonds at $3 \text{ \AA}$).^{15,45} The differential PDF shows a main peak at $2.37 \text{ \AA}$, 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 Y³⁺ and YSO₄⁺ aqueous solutions (Fig. 1). Another peak is present at $1.7 \text{ \AA}$, 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 $3.48 \text{ \AA}$, 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 Fig. 1A). This peak may also correspond to a Y-Al interatomic distance, which would be consistent with the formation of an inner-sphere complex, 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), pure basaluminite (B-pure) and differential PDF (d-PDF). The d-PDF spectrum has been amplified ($\times 3$) for visualization purposes.

The k^3 -weighted EXAFS spectra for the solid references B-YSO₄-ads, B-Y-ads, B-Y-cop and A-Y-ads (Fig. 3) are indistinguishable and differ from the aqueous Y-sol and YSO₄-sol spectra in that a slight oscillation becomes visible at 5-6 $\text{\AA}^{-1}$. In the B-YSO₄-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 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 Fig. 3) may be related to the presence of an Al backscatterer, rather than to a signal from an 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.

[A1]

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) and solid standards (basaluminite sorbed with YSO₄. (B-YO₄), basaluminite sorbed and coprecipitated with Y: B-Yads and B-Ycop, respectively) and

aqueous solution (free ion and sulfate complex: Y-sol and YSO₄-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 YSO₄-sol (solution of Y with SO₄) standards as the most representative references (results in Table 3). The arrows indicate a frequency present in the solid standards.

Based on the previous information of the aqueous species and on the thermodynamic model of REE sorption,¹⁷ the B-YSO₄-ads EXAFS signal was fitted with three models of different geometries of the YSO₄⁺ aqueous complex adsorbed onto basaluminite surfaces via inner-sphere complexes (Fig. 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.

Figure 4. Atomistic representations of the three models of YSO₄ aqueous complex adsorbed on the basaluminite-water interface. The different atomic positions of YSO₄ to octahedral-Al are used to fit the EXAFS signal of the B-YSO₄ sample. The three

models show different inner-sphere surface complexes: (A) monodentate, (B) bidentate mononuclear and (C) bidentate binuclear.

The EXAFS fits for B-YSO₄-ads for the different models and the calculated parameters are given in Fig. 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 another sources: The major aqueous species in solution was YSO₄⁺, 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 YSO₄⁺ aqueous complex.¹⁷ With this information the fit was performed assuming S and Al coordination numbers equal to 1 and 2, respectively, as it is shown in Fig. 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 fix coordination number of 8. The second shell was fitted yielding a Y-Al distance at 3.52 Å with a fixed coordination number of N = 2, and a Y-S distance at 3.33 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 (Fig. 4A). The second model, the bidentate binuclear inner-sphere complex configuration, gave poorer results without structural significance and with higher χ^2_v values (Table 2), so it was discarded. The third model was the bidentate binuclear, 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 an 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.

Overall, the monodentate inner-sphere surface complex gave the best fit results, which was in accordance to the thermodynamic sorption model. Moreover, the bidentate binuclear inner-sphere surface complexes yielded also a good fit with similar χ^2 values than the monodentate hypothesis, making this configuration also possible (Fig. 4C). In both fits, the distances between Y-S are similar, 3.33, 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.

Figure 5. (A) The k^3 -weighted EXAFS spectra at the Y K-edge of the basaluminite with YSO4 sorbed (B-YSO4 reference) and (B) its Fourier transform amplitude. The experimental and fitted curves are shown in black and red, respectively.

Table 2. 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. indicates 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^2_v
1*	1 st 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)		
	2 nd 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	1 st shell	Y-O	10 (1)	0.012(2)	-6(2)	2.33 (1)	8	402
	2 nd 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	1 st shell	Y-O	10(1)	0.013(1)	-4(1)	2.33(1)	8	334
	2 nd 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)		

The EXAFS of the B-YSO4-ads standard was also fitted with the same three atomistic models presented in Fig. 4 but without sulfate included (Fig. 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 Table 2 and Table 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 -Al₂O₃ to form inner sphere complexes.⁴⁷ 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. 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 -Al₂O₃ 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 $\geq$ 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 at 3.38 Å. These EXAFS results were complemented by time-resolved laser fluorescence spectroscopy (TRLF) 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 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 at 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 $\sim 8 \pm 1$ 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 Fig. 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 solid references (B-YSO4-ads, B-Y-ads, B-Y-cop and A-Y-ads). They have a shoulder at $\sim 6.5 \text{ \AA}^{-1}$, indicating a higher frequency which is absent in the aqueous samples (see arrow in Fig. 3).

Based on the PCA analyses (see Chapter S3), the reconstructed spectra indicated that only two components were required to describe the samples (Fig. S4). The two most likely Y species identified by target transformation of the standard spectra, were the B-YSO4-ads and B-Y-ads references (Fig. 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-YSO4-ads and YSO4-sol (Fig. 3A, upper part) to quantify the proportions of different Y species in the waste samples. The use of these 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-YSO4-ads reference (with the exception of sample W-Alm-C3-8, for which the LCF indicated equal proportion of both YSO4 presented as inner sphere 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-oxyhydroxisulfate, due to the presence of small amount of Fe in the solids. Specifically, samples from Almagrera column (W-Alm-C3-8 and W-Alm-C3-9) presented higher Fe concentration than samples from Monte Romero treatment. REE can be also 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-YSO4-ads.

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-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
χ^2	133	154	371	392

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-SO₄

ion pair with a monodentate configuration, with an Y-S interatomic distance of 3.5 Å. Results from 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 into basaluminite by itself, due to the low sensitivity to discern between Al and S neighbors. Rather than this, the EXAFS fitting, together with the PDF, can confirm the strong interaction and the formation of inner-sphere surface complexes of Y onto 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 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 HREE (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 to enhance a selective recovery of REE from AMD wastes and thus to generate an economic value of the waste generated during the neutralization of AMD-affected waters.

Associated information

Supporting information. The supporting information contains 1) five chapters with detailed description of synthesis of reference materials, analytical procedures and aqueous speciation calculations, synchrotron experiments and data analyses, molecular dynamics simulations and the Python code used to generate PDF from AIMD simulations; 2) three tables describing samples used for EXAFS measurements and the modeling parameters from EXAFS fitting; and 3) four figures illustrating fitting of EXAFS spectra.

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