



The potential role of aluminium hydroxysulphates in the removal of contaminants in acid mine drainage



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ABSTRACT

Sorption of trace elements onto poorly-crystalline Al-hydroxysulphate minerals from acid mine drainage (AMD) has received less attention compared to similar Fe(III)-phases because the former are less abundant in many mine drainage environments. In addition, Al-hydroxysulphates precipitate at a higher pH, so their sorption characteristics could be masked or less significant after sorption of trace elements to Fe minerals, which form at lower pH. In this study, oxidation and titration experiments were conducted with Fe(II)-rich AMD solutions under atmospheric and anoxic conditions to elucidate, individually, the sorption capacity of trace elements in solution by Fe and Al-hydroxysulphates. Under atmospheric conditions, precipitation of Fe(III) as schwertmannite, led to total removal of Fe, As, Cr and Pb in solution and 50% of Al. Subsequently, contaminant-depleted solution began to be controlled by precipitation of basaluminite, which acted as an effective sink for the remaining Al, Cu and Si. On the contrary, under anoxic conditions, neutralisation of Fe(II)-rich solutions led first to the basaluminite precipitation, keeping all Fe available in solution and unveiling a heretofore unknown affinity for As and Cr. Basaluminite retains 60% of As in solution compared to 100% removal of As by schwertmannite. However, the sorption capacity of basaluminite is even more significant than that of Fe-phases, considering that Al concentrations in solution were much lower than those of Fe. These findings give new insights into the processes controlling contaminant mobility in anoxic environments (e.g., the bottom of AMD-affected water reservoirs) and pose new opportunities for treatment strategies.

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1. Introduction

Contamination of receiving waters and sediments by acid mine drainage (AMD) is one of the main environmental problems associated with mining of sulphide-bearing ore deposits (Nordstrom, 1982a; Nordstrom and Alpers, 1999). These acidic waters have high concentrations of sulphate and metal(oid)es and result from the continuous exposure of sulphide-rich mining wastes, derived mainly from coal fields or massive sulphide ores, to oxygen and water. Pollution by AMD is a serious environmental problem affecting active and abandoned mining areas around the world. Examples of contamination by AMD are described in detail in the Appalachian coalfields (USA) (Powell, 1988; Herlihy et al., 1990), in the Gangreung coalfield (Korea) (Yu and Heo, 2001; Kim and Chon, 2001) and in the Iberian Pyrite Belt (IPB; Iberian Peninsula) (Leblanc et al., 2000; Sáinz et al., 2002; Sarmiento et al., 2009), among many others. The IPB is one of the most strongly AMD-affected areas worldwide (Nieto

et al., 2013). In addition, processes that form AMD can operate within mine waste materials long after mining has stopped and AMD leachates can persist for many decades or even centuries after mine operations cease (Younger, 1997).

Acid mine drainage is characterised by high concentrations of sulphate, iron (from sulphide mineral oxidation, mainly pyrite) and aluminium (from weathering of the host rocks), in addition to the presence of other trace elements. In cases with limited oxygen renewal, such as in underground shafts, the emerging acidic water is depleted in oxygen, and thus contains high concentrations of Fe(II). In atmospheric conditions, the presence of oxygen and, mainly, the activity of extremophile microorganisms catalyse the total oxidation of Fe(II) to Fe(III) after a few metres of flow (Nordstrom and Alpers, 1999). Under such conditions, both AMD hydrochemistry and mineralogy are controlled mainly by the SO₄-Fe(III) and SO₄-Al systems (Bigham et al., 1996; Nordstrom and Alpers, 1999).

In AMD-affected streams, high concentrations of ferric iron and sulphate favour the spontaneous precipitation of schwertmannite [Fe₈O₈(OH)_(8-2x)(SO₄)_x·nH₂O; with x varying from 1 to 1.75], a

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poorly-crystalline Fe-oxyhydroxysulphate (Bigham et al., 1990, 1994; Yu et al., 1999; Fernandez-Martinez et al., 2010). Schwertmannite has a high capacity to remove trace elements, particularly As and Cr, from AMD solutions (Acero et al., 2006). The oxidation state seems to be an important factor in the removal processes. For instance, arsenic mobility may be controlled by As(V) sorption onto schwertmannite under acidic conditions (Burton et al., 2009; Maillot et al., 2013). Consequently, the spontaneous nucleation and growth of schwertmannite can lead to a natural attenuation of contamination (Schwertmann et al., 1995; Courtin-Nomade et al., 2003; Fukushi et al., 2003). The precipitation of schwertmannite is also induced by the progressive increases of pH due either to AMD mixing with pristine receiving waters or to alkali addition in AMD treatment systems. With the progressive increase of pH, after all aqueous iron has precipitated, aluminium starts precipitating as basaluminite [$\text{Al}_4(\text{SO}_4)(\text{OH})_{10}\cdot 4\text{-}5\text{H}_2\text{O}$], a poorly-crystalline Al-hydroxysulphate (Hollingworth and Bannister, 1950; Nordstrom, 1982b; Frakas and Pertlik, 1997). Basaluminite has been less studied than schwertmannite, though it is also known that it has a strong potential to remove elements such as Cu and Si (Nordstrom and Alpers, 1999; Bigham and Nordstrom, 2000).

The precipitation sequence of schwertmannite followed by basaluminite as the pH is increased by alkali addition, as well as their influence on the trace element mobility, has been reported in laboratory titration experiments (e.g., Lee et al., 2002; Sánchez-España et al., 2011) and field treatment systems (Caraballo et al., 2011; Macías et al., 2012). The alkaline neutralisation of Fe(III)-Al-SO₄-rich AMD solutions exhibits two buffers at pH ranges between 2–4 and 4.5–6 that are related to Fe and Al hydrolysis, and subsequent precipitation of schwertmannite and basaluminite, respectively. In this precipitation sequence the sorption capacity of trace elements by basaluminite evidently is masked by the previous schwertmannite precipitation. No study concerning the behaviour of contaminants during the exclusive precipitation of basaluminite (i.e., avoiding schwertmannite formation) has been reported in the scientific literature.

To help bridge this gap, the present study reports the results of AMD neutralisation experiments performed in the laboratory under two different conditions: (1) under atmospheric conditions, to simulate the oxidation of Fe(II) to Fe(III) and the natural precipitation of Fe in the first instance, and the subsequent formation of Al-hydroxysulphates; and (2) under anoxic conditions, using a Fe(II)-rich AMD solution, to precipitate first the Al-hydroxysulphates so their reactivity with the natural contaminants present in AMD can be isolated. Results from the two experiments were compared to identify the individual trace element removal capacities of poorly-crystalline Fe and Al phases. This is relevant not only for AMD-affected receiving waters, but also for other environments where poorly-crystalline precipitates as basaluminite are present, such as acid-sulphate soils (Adams and Rawajfih, 1977; Jones et al., 2011). However, understanding the geochemical processes controlling metal mobility during Al and Fe precipitation required further detailed characterisation studies beyond chemical analyses. The low crystallinity of these precipitates limited the use of conventional X-ray techniques for their mineralogical characterisation. In this study, high-energy X-ray diffraction (HEXD) using synchrotron-based radiation helped to overcome this obstacle.

2. Materials and methods

2.1. Field site and sampling description

Laboratory experiments were conducted using Fe(II)-rich acidic waters collected from an underground mine gallery at the Perrunal abandoned mining district (IPB, southwest Spain). Some representative samples were collected in September 2012, during the dry season, when the stream flow was approximately 1 L s^{-1} . The pH, redox potential, electrical conductivity (EC), dissolved oxygen (DO), temperature and Fe(II)/Fe(III) speciation were measured on site. The samples were

collected in airtight high density polyethylene 5 L containers, previously washed in the acid stream, and stored without exposure to air, in dark conditions and cooled to prevent Fe(II) oxidation. After collection, the samples were rapidly transported to the laboratory where the titration experiments were started immediately. An aliquot (60 mL) was filtered through a 0.45- μm nylon filter, acidified with HNO_3 to $\text{pH} < 1$ and stored in plastic vials at 4 °C for further chemical analysis.

2.2. Neutralisation experiments

Two neutralisation experiments by alkaline titration of the Fe(II)-bearing AMD samples were conducted in the laboratory under different conditions:

- 1) Oxygen-saturated atmosphere (atmospheric conditions): the experiment consisted firstly of a spontaneous oxidation of Fe(II) to Fe(III) (i.e. pre-titration oxidation), followed by a titration. To this end, a volume of 4 L of acid water was transferred to a glass beaker. The experiment was monitored using two, 20 mL aliquots that were retrieved daily; one aliquot was used to measure pH, redox potential, EC, temperature, DO and Fe speciation, and the other aliquot was used for chemical analysis after filtration and acidification. The experiment was performed at room temperature (25 °C) while monitoring water loss due to evaporation. When all Fe(II) in solution was oxidised to Fe(III), an aliquot was filtered through a 0.1 μm filter and used to carry out the titration by alkaline addition, in duplicate: (1) 100 mL of Fe(III)-AMD solution were used to obtain the titration curve, and (2) 200 mL of Fe(III)-AMD were titrated to sample the solution at desired pH values (mainly before, during and after the different buffering regions). The titration consisted of adding dropwise a 0.01 M $\text{Ca}(\text{OH})_2$ solution while constantly stirring the sample using a magnetic bar. The pH was continuously monitored using a pH-metre. Solution samples (ca. 20 mL) were filtered and acidified for major and trace elements analysis.
- 2) Oxygen-free atmosphere (anoxic conditions). This experiment was performed in such a way as to maintain the Fe in its ferrous state throughout the experiment. To this aim, the AMD solution was deaerated by continuously bubbling N_2 through the sample for 1 h and then storing the sample inside a nitrogen-filled glove box to prevent oxidation during the experiment. The oxygen concentration in the glove box was less than 0.4% during the experiment. As in the experiment under atmospheric conditions, though without the first oxidation step, the Fe(II)-AMD solution was first filtered and then titrated using a previously deoxygenated 0.01 M $\text{Ca}(\text{OH})_2$ solution, in duplicate: (1) an aliquot of 100 mL was used to obtain the titration curve and (2) another aliquot of 200 mL was used for sampling the solution at desired pH values during the neutralisation. The solution samples (ca. 20 mL) were filtered for Fe speciation analysis and acidified inside the glove box for analysis of major and trace elements. After obtaining the titration curve, the final suspension of neutralised acid water and the newly-formed precipitates were exposed to atmospheric conditions without stirring to induce their spontaneous oxidation (i.e. post-titration oxidation). Both pH and Fe speciation were also monitored during this oxidation and solution samples (ca. 20 mL) were collected, filtered and acidified for major and trace elements analysis.

Several newly-formed solids were observed and collected in each pH-buffering region during the neutralisation experiments. These new solids were one precipitate from the pre-titration spontaneous oxidation, three precipitates from the titration under atmospheric conditions, two precipitates from the titration under anoxic conditions and two precipitates from the post-titration spontaneous oxidation. The latter samples were examined to determine any phase transformations during the oxidation. All these solids were separated by centrifugation and then rinsed several times with ultrapure water.

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