Surface chemistry of iron oxides formed by neutralization of acidic mine waters: Removal of trace metals

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ARTICLE INFO

ABSTRACT

Secondary iron minerals are important in mining areas as they are natural scavengers of many contaminants. Thus, aluminium and iron oxides derived from acid mine drainage determine the fate of trace metals commonly found in mining areas. They mainly do this via sorption processes, which prevent leaching of the metals and contamination of surface and groundwater.

In the present study, abiotic precipitates were obtained from samples of acid drainage water collected from an abandoned copper mine. Characterization of the precipitates revealed that schwertmannite was the dominant iron mineral phase present. Retention of Cu, Cd, Ni and Pb by natural iron precipitates was compared with retention of the same elements by synthetic analogues. The study findings indicate that the natural abiotic precipitates have a higher retention capacity than their synthetic analogues. Thermodynamic modelling was used to predict the geochemical behaviour of the trace metals in the presence of iron precipitates. Inclusion of adsorption and precipitation reactions in the models yielded a good description of the degree of attenuation of adverse effects of the trace metals. Under acidic conditions, the schwertmannite-like particles initially present in the natural precipitates evolve towards more crystalline mineral phases. This transformation process is accompanied by the release of sulphate ions into the solution and by a decrease in trace metal sequestration.

1. Introduction

Mining activities are a worldwide source of contamination that represents a major threat to biota and humans via the effects it has on soils and aquatic systems. The formation of acid mine drainage (AMD) implies the weathering and oxidation of iron sulphide minerals in mining areas and the formation of large amounts of secondary iron precipitates. In addition, AMD contamination of surface waters usually results in low pH values and high concentrations of sulphate and trace metals (Nordstrom, 2011). The trace metals usually found in areas affected by AMD are harmful when present as mobile and bioavailable forms, as these can readily accumulate in benthic organisms and/or plants.

The formation of secondary minerals in areas affected by AMD determines the behaviour of the different trace elements as it leads to immobilization of the elements via surface adsorption or co-precipitation mechanisms. The AMD precipitates formed in river terraces, banks and beds (mainly iron and aluminium oxyhydroxysulphates) can thus act as both sinks and sources of pollution (Asta et al., 2010; Parviainen et al., 2015; Sarmiento et al., 2011). The nature and composition of the

secondary iron minerals is determined by the physico-chemical characteristics of the aqueous phase. Thus, jarosite is formed at pH < 3, schwertmannite is commonly formed at pH 3–4, and ferrihydrite and goethite are formed at neutral pH (Bigham and Nordstrom, 2000). Due to their metastable nature, some of the mineral phases present in AMD systems may evolve within weeks or months towards more crystalline mineral phases, depending on the pH, E_h and temperature of the system (Acero et al., 2006; Antelo et al., 2013; Bigham et al., 1996; Kumpulainen et al., 2007).

In the last decade, various studies have focused on characterizing the adsorption behaviour of secondary iron minerals and their synthetic analogues (Antelo et al., 2012; Asta et al., 2009; Burton et al., 2009; Carrero et al., 2017; Jönsson et al., 2006; Webster et al., 1998). These minerals are known to attenuate trace metal contamination via surface adsorption and co-precipitation processes (Martínez and McBride, 2001; Regenspurg and Peiffer, 2005). Co-precipitation of trace elements during the formation of synthetic schwertmannite analogues enhances the thermodynamic stability of the mineral and may also increase its surface reactivity (Antelo et al., 2013). Moreover, the presence of adsorbed or structural sulphate groups on the surface of ferrihydrite and

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schwertmannite increases the retention of trace metals through the formation of ternary complexes (Webster et al., 1998). However, few studies have been conducted with natural analogues, such as bed sediments or iron minerals formed in iron-rich AMD waters by biotic or abiotic precipitation processes (Burgos et al., 2012; Lee et al., 2002; Sidenko and Sherriff, 2005). Data obtained with synthetic analogues do not reflect natural behaviour as in natural settings, iron oxides are formed in multicomponent systems: e.g. AMD waters usually contain Fe, Al, S, and other trace metals and metalloids. Co-precipitation is thus likely to occur and may lead to the formation of different secondary minerals and to the presence of impurities that may affect the stability and reactivity of the different mineral phases. This is a key factor in relation to the natural attenuation of ecosystems affected via AMD by high concentrations of trace metals and their potential mobilization to unaffected systems.

The specific objectives of the present study were as follows: 1) to identify and characterize the iron precipitates formed via abiotic neutralization of acidic waters from an abandoned copper mine; 2) to compare the binding behaviour of copper, lead, nickel and cadmium on these precipitates and on synthetic analogues; 3) to evaluate the capacity of surface complexation models to predict metal binding on the abiotic iron precipitates; and 4) to analyze the mineral stability of the abiotic precipitates and the possible release and mobilization of copper ions into aquatic systems.

2. Materials and methods

2.1. Field sampling

Mine water samples were collected at the abandoned Touro copper mine in Galicia (NW Spain, 42° 52′ 34″ N 8° 20′ 40″ W) in the summer of 2012. The main ore minerals found at the mine, which was operational between 1974 and 1988, include chalcopyrite and pyrrhotite. Remediation and environmental monitoring activities have been conducted at the most critical sites (Álvarez et al., 2011) during the last 15 years. A water sample was collected from a stream (WS) flowing across the mine area (Fig. 1), and another sample was collected from a mine tailing pond (MTP). Both samples were immediately filtered through 0.45 μm Millipore filters in the field, and subsamples were acidified with 1% HNO_3 for subsequent metal analysis. Parameters such as pH, temperature, electrical conductivity and dissolved oxygen were measured *in situ*. The samples were transported to the laboratory and stored at 4 °C until analysis. Trace metals were determined by inductively coupled plasma-opical emission spectrometry (ICP-OES) (Perkin–Elmer Optima 3300DV), and the concentrations of Fe and Al were determined by atomic absorption spectroscopy (Perkin-Elmer 1100B). The sulphate and chloride contents were determined by standard methods (Clesceri et al., 1998).

2.2. Precipitation and characterization of iron secondary minerals

The precipitates were obtained by abiotic neutralization of AMD waters, following a similar procedure to that reported by Burgos et al. (2012). In these experiments, the pH of the AMD water was gradually increased to pH 4.4–4.6 (at a flow rate of 1 mL/min during 3 h) and was then maintained constant for a 15-day period by addition of aliquots of a freshly prepared 1 M KOH solution. During the precipitation process, the samples were continuously stirred and N_2 was bubbled into the KOH solution and the sample vessels. Most of the Fe(III) present in the aqueous solution precipitated along with other metal cations. All ions that did not co-precipitate were washed out by dialysis through membranes (Spectrum Labs MWCO 1000). The washing step was considered complete when the conductivity of the water fell below 10 μS cm^{-1}. A fraction of the final suspensions was freeze-dried to obtain solid samples for characterization of the iron precipitates, while the remaining fractions were stored as suspensions at 4 °C for the adsorption

experiments. The concentration of iron precipitates in the suspension was determined gravimetrically. All the adsorption experiments were conducted within a month after obtaining the precipitates.

The nature of the precipitates obtained from the AMD water was analysed by powder X-ray diffraction (XRD) (Phillips PW1710 X-ray diffractometer). Measurements were made between 10° and 70° 2θ, with a step size of 0.02° and a counting time of 6 s per step. Electrophoretic mobility was measured in suspensions of 0.05 g/L iron precipitates in 0.01 M KNO_3, in a particle analyzer (Malvern Zetasizer Nano ZS90). The isoelectric point (IEP) was determined by titrating the samples over a wide range of pH (4–11) (with a Malvern MPT-2 Multi-Purpose Titrator). The pH of the suspensions was adjusted using 0.01 M HNO_3 or KOH solutions as titrants. Three different measurements were made at each pH and the average electrophoretic mobility values were calculated. The zeta potential values were calculated from the electrophoretic mobility values by using the Smoluchowsky equation. Special care was taken to avoid contamination of the samples with CO_2, by maintaining the suspensions and the titrant solutions under N_2 atmosphere. The chemical composition of the precipitates was analysed after digestion of 0.05 g of the solid samples in 50 mL of 6 M HCl for 3 h. The Fe, Al, and trace metal contents were measured by ICP-OES, whereas the sulphate content was determined by a turbidimetric method (Clesceri et al., 1998) in a JASCO V-530 UV/VIS spectrophotometer.

2.3. Preparation and characterization of synthetic analogues

Two schwertmannite preparations (Sch-S1 and Sch-S2) were produced following a similar procedure to that described by Bigham et al. (1990). Briefly, 10.8 g of $FeCl_3·6H_2O$ and 3 g of Na_2SO_4 were added to 2 L of preheated (60 °C) distilled water. The orange/red precipitates thus obtained were heated at 60 °C for 12 min and then cooled to room temperature. The precipitates were then dialysed at room temperature in double-distilled water for 33 days and the final products were freeze-dried.

The synthetic schwertmannites were characterized by XRD. Electrophoretic mobility was determined as described above for schwertmannite suspensions of 0.1 g/L prepared in 0.01 M KNO_3. The Fe and SO_4 contents in the schwertmannite preparations were determined following the same procedure as for the iron precipitates, i.e. digestion of the solid samples with 6 M HCl.

2.4. Adsorption experiments

Batch experiments were conducted to obtain the adsorption envelopes for Cu, Pb, Ni and Cd in the range pH 4–9 by using the AMD precipitates. The synthetic schwertmannite were used to obtain additional adsorption envelopes for Cu. Furthermore, the adsorption envelope for Cu was obtained with a synthetic ferrihydrite prepared by Antelo et al. (2015). In all cases, suspensions of 0.5 g/L were prepared in 20 mL of 0.1 M KNO_3 in polyethylene vessels. Adequate volumes of metal stock solutions were added to yield a metal concentration 1 mM in the suspensions. High concentrations of heavy metals were selected to enable analysis of the attenuation capacity of the precipitates and also to simulate highly polluted waters. The pH of the suspensions was adjusted to within the working range by addition of small volumes of 0.1 M HNO_3 or KOH solutions. Preliminary kinetic experiments showed that a minimum time of 6 h was required to achieve pseudo-equilibrium with AMD or synthetic analogues (hereafter we refer to equilibrium conditions to simplify the discussion). The suspensions were shaken continuously during the equilibration period; the pH was measured periodically and readjusted when necessary. The suspensions were then filtered through 0.45 μm Millipore filters and the metal concentrations corresponding to the amount remaining in solution were measured in the filtrates by ICP-OES. The amount of adsorbed metal cation was determined as the difference between the total amount added and the