Arsenic Fate During Schwertmannite Transformation: an EXAFS Approach

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INTRODUCTION.

The cycling of arsenic in Acid Rock Drainage (ARD) is controlled by several factors, such as mineralogy of the primary ores and enclosing rocks, weathering conditions and hydrological variability. Moreover, precipitates newly formed from ARD, such as jarosite (Jrs), schwertmannite (Sch) and goethite (Gt) may play a key role in the removal of trace elements from solution, and there exists an extensive literature describing the retention of arsenic by these minerals. However, most of arsenic retention studies have been performed in laboratory and with synthetic monomineral phases, whereas a mixture of oxyhydroxisulfats is commonly found associated in many ARD, and therefore it is not clear the particular role of each of these three mineral phases in the As cycle. The mineral phase containing arsenic and the type of link to the solid structure (sorption vs coprecipitation) appears to be relevant in the future remobilization of arsenic (Burton et al., 2007).

Recent studies have shown that Sch is a metastable phase, and has been found in the laboratory to transform into Gt and Jrs in weeks or months. Acero et al (1996) conducted a laboratory experiment consisting in aging monominerallic natural Sch under controlled conditions, and compared the results with field samples of fresh and aged precipitates in an acid stream. In the laboratory, natural Sch was kept in contact with its coexisting acid water in a flask with a solid-liquid mass ratio of 1:5 for one year. During this time, the pH of the solution dropped from 3.1 to 1.7 and the concentrations of sulfate and Fe increased. During the first 164 days, Sch transformed into Gt plus H_3O-Jrs but, from that moment, goethite was the only product to form. Arsenic was depleted in solution during the first stage as Sch transformed into Gt plus H_3O-Jrs. On the contrary, the transformation of Sch to Gt (with no Jrs) during the second stage released arsenic to the solution. This seems to suggest that Gt is a less efficient arsenic sink than Sch and Jrs. However, another possible explanation for the As release in the last part of the aging experiment is the switch of As(V) aqueous speciation from $H_2AsO_4^-$ to $H_3AsO_{4(aq)}$ predominance at pH around 2.5 (Dixit and Hering, 2003), which could contribute to the As desorption from Gt as pH decreases.

The relative ability of Jrs and Gt to retain arsenic also remains unclear in the literature. Whereas some earlier studies claim that As can remain immobilized in Jrs by replacing sulfur in sulfate tetrahedra (Savage et al. 2000, 2005), other works show that As is retained preferentially in Gt over Jrs (Strawn et al., 2002). To solve the uncertainties on the role of Sch, Jrs and Gt in the arsenic cycling, we performed EXAFS analysis of samples taking from different stages during the aging experiment described by Acero et al (2006). This study will be completed with the EXAFS analysis of samples from field terraces taken at different depth. The main objective of our work is the study of arsenic speciation in solids during Sch transformation.

SAMPLES AND METHODS.

A subset of four samples from previous study (Acero et al., 2006) was used in this work. Mineralogical transformations observed during aging experiment are shown in Fig. 1. X-ray absorption spectra were collected at the As K-edge at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on beamline BM8 (Gilda). Samples were prepared as pellets and they were measured in fluorescence mode with a Ge 13-element detector. All steps of the XAFS data reduction were performed using the WinXAS 95 1.1 software package. The spectra were analyzed by linear combination least-squares fitting (LSF) procedures of model compounds using the software package form the beamline 10.3.2 for the Advanced Light Source (ALS), Berkeley, USA. The quality of the fit was quantified by the R parameter as defined in Fig. 2. The set of model compounds used for the EXAFS fitting of sample spectra included As(V) adsorbed and co-precipitated with synthetic Sch, Gt and Jrs. These samples were analysed in the same run under identical experimental conditions. The oxidation state of As was determined from XANES analyses using As(III) and As(V) standards. As(V) is the only As species present in these samples.

RESULTS.

A LSF procedure was performed on the EXAFS spectra of the four selected samples (t=0 days, 105 days, 148 days and 237 days). This procedure has already been successfully used in determining As speciation in environmental samples. The fitting procedure yielded the relative proportions listed in Table 1. In fresh surface precipitates (t=0 days) As is present sorbed and co-precipitated with Sch. These mechanisms have been described in the literature and identified as efficient scavengers of arsenate. A larger proportion of As(V) present in the solid is included in the Sch structure.

The presence of Gt is confirmed by XRD 105 days after the start of the experiment. Four components (Table 1) can explain the EXAFS spectra. An important proportion of As in the solid phase is co-precipitated with Gt and adsorbed onto Jrs (Fig. 2). Batch experiment has shown that during this transformation As is retained in the minerals and no As increasing concentrations are observed in solutions in contact with the solids. The XRD spectra do not reveal the presence of Jrs at this time, likely because the
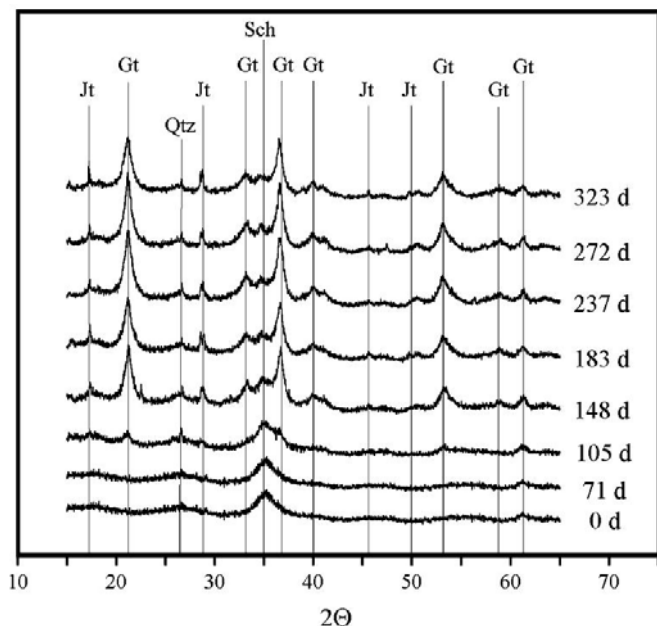
fig 1. *The XRD patterns for samples taken at different times (in days) during the laboratory experiment on Sch aging. The diagrams show the evolution from pure Sch (0 day) to Gt plus Jt (Jarosite) (323 days), Qtz (Quartz). Taken form Acero et al., 2006.*
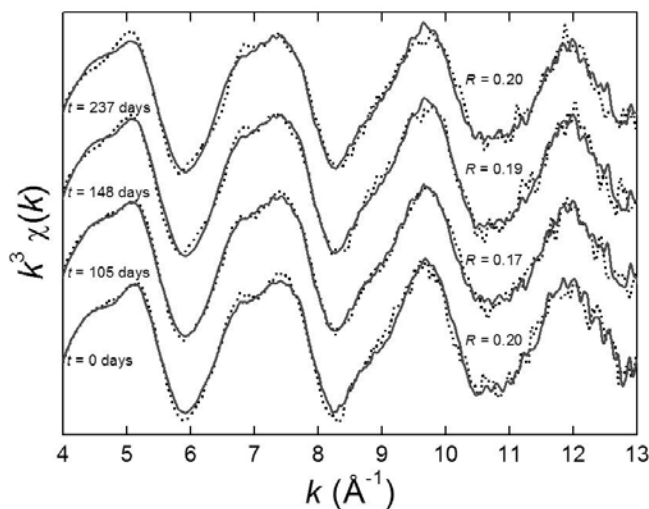

fig 2. *The EXAFS spectra and their least square fittings as a function of aging time. Experimental and calculated data are represented in dotted and solid lines respectively, and* $R = \sum \left| y_{obs} - y_{fit} \right| / \sum \left| y_{obs} \right|$.

to the liquid phase. Jarosite appears as a very instable trapping phase and As sorption onto Gt is not observed likely because the very low pH in these streams does not favour As(V) adsorption processes. More data about As(V) adsorption onto goethite at pH<4 are needed to explain these very acidic environments.

Model Compounds (%)	0 days	105 days	148 days	237 days
As sorbed on Sch	32	29	24	22
As co-prec. with Sch	62	42	40	43
As sorbed on Gt	-	-	-	-
As co-prec. with Gt		20	16	30
As sorbed on Jrs		14	11	10
As co-prec. with Jrs	-		15	-

Table 1. Quantitative As speciation in samples estimated by LSF of EXAFS spectra. The sum of percentages of As species is not always equal to 100% because a tolerance of ±10 % is admitted.

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amount of this mineral is not enough for the experimental resolution (~ 5%). After 148 days of experiment, the presence of Gt and Jrs is evident in the XRD spectrum. In this case five components were used to match the EXAFS diagram. Concerning the new solid phases, As is mainly included in Gt and Jrs structure and a small proportion is linked as sorbed species in Jrs. Examining the sample at t=237 days we can observe that Gt continue to trap As in its structure but Jrs became a less important scavenger. It is worth noticing that As adsorption on Gt is a very common trapping mechanism but it is not relevant in this very acidic mining site.

CONCLUSIONS.

Taking into account the observed evolution of the solid phases, the two main periods previously mentioned can be interpreted as follows. (1) From 0 to 164 days the transformation of Sch into H_3O-Jrs and Gt retains As (V) sorbed onto Jrs and included in the mineral structure of Gt and Jrs. During this period Jrs acts as an As(V) scavenger and for this reason it is not released into the solutions. (2) From 164 to 237 days during the transformation of Sch into Gt, As(V) is co-precipitated with the new solid phase. However, Gt does not appear as an efficient scavenger and As is then released