

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Dissolution of natural scorodite in a mine waste: evidence of nanosized ferrihydrite formation and its role as As carrier	<b>Experiment number:</b> CRG 25-01 849
<b>Beamline:</b> BM25A	<b>Date of experiment:</b> from: 17/11/2013 at 08:00 to 19/11/2013 at 08:00	<b>Date of report:</b>
<b>Shifts:</b> 9	<b>Local contact(s):</b> Dr Eduardo Salas	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b>  S. Serrano*, F. Garrido* M.A. Gómez-Gonzalez*, Instituto de Ciencias Agrarias, CSIC, Spain  P. A. O'Day, University of California, Merced, US  E. Bolea and F. Laborda, Departamento Química Analítica, Universidad de Zaragoza, Spain.		

### Report:

Scorodite occurs often as a secondary mineral in oxidized waste rocks and mine tailings rich in arsenopyrite. Considered the least soluble arsenate phase in many mine tailing systems and with a low dissolution rate, scorodite remains at mine waste sites after many years of weathering in natural conditions. However, under strongly acid conditions scorodite congruently dissolves, releasing equimolar concentrations of As and Fe, while at higher pH, it does incongruently, forming ferrihydrite and arsenate. Arsenic adsorption on ferrihydrite resulted from incongruent dissolution of scorodite has been proposed in the literature as the controlling factor in the solubility and subsequent release of As to the media. In spite of it, little is known about As mobilization associated to the nano-ferrihydrite, precipitated after scorodite dissolution in mine waste. Because of the colloidal size of this ferrihydrite, we hypothesize that ferrihydrite could act as As carrier and, therefore, increases As mobility and contamination of surface or subsurface water bodies. Most of the studies about natural colloids and their role as carriers of toxic elements are based on microscopic techniques and thus, no conclusive information about the chemical mechanism between the contaminant and the colloidal particles could be address. Additional research at a molecular scale is needed to evaluate the stability of these interactions and assess the environmental risk associated to them. As a fundamental step within the research project CGL2010-17434 financed by the Spanish National Research Plan, our experiment aimed to study scorodite dissolution at different pH conditions to characterize the dissolution products and determine the stability of the As-Fe particles interactions at a molecular scale, information that is key to predict the potential environmental impact of these As-colloid associations

### Experimental methods

All our experiments were performed using a scorodite-rich waste material (waste pile – WP) dumped outside in an abandoned smelting factory located in Guadalix de la Sierra (Community of Madrid, Spain), in which arsenopyrite encapsulated in quartz was processed for wolfram extraction during the Second World War.

Dissolution experiments at different pH conditions (3, 4, 5, 6, 7) and reaction times (6, 12, 24, 36, 48, 60, 72 hours and 7, 15, 30 days) were performed using batch technique with this scorodite-rich waste materials at 1:10 solid:solution ratio. Samples of the colloid fraction released after the dissolution experiments were isolated on the basis of a centrifugation protocol already tested from previous experiments (see CRG\_25\_01\_817) aiming to separate particle size fractions larger than the target size ( $< 1\mu\text{m}$ ). The dissolved fraction ( $< 10\text{ nm}$ ) was obtained by ultrafiltration of the  $< 1\mu\text{m}$  fraction through a ultrafiltration membrane. The ultrafiltration membranes were removed from the holders and colloids measured by XAS. Colloidal suspensions were also placed on Ni grids for subsequent Transmission Electron Microscopy (TEM) observations.

## Samples and spectra collected

During our experiment, As and Fe k-edge EXAFS spectra of three colloid samples isolated from the scorodite-rich waste suspensions obtained after the following experimental conditions, pH 3 and 7 days, pH 6 and 7 days, and pH 6 and 6 hours, were measured on bending-magnet BM25A beamline (SpLine) (6 GeV, 100 mA, Si(111) monochromator crystals) in fluorescence mode using a 13-element Si(Li) solid state detector with the sample at room temperature. A total of 72 As/Fe spectra (12 scans per colloid sample and element) are currently being analyzed using the computer packages ATHENA (Ravel and Newville, 2005) for linear combination fits. Background was subtracted using a linear fit through the pre-edge region and the Autobak routine in Athena for the spline fit through the EXAFS region. Arsenic XANES spectra were fit by linear least-squares combination fits of reference compounds to verify the As oxidation state.

In addition to the colloid samples, preliminary Fe XANES spectra of six bulk sediment samples collected in an area next to the waste pile were measured.

## Results

Preliminary As and Fe XAS analysis of the colloid fraction after isolation of the colloids on ultrafiltration membranes indicated only partial dissolution of Scorodite (Figure 1 and Figure 2), compare to the untreated WP sample and the scorodite spectra.

Figure 1

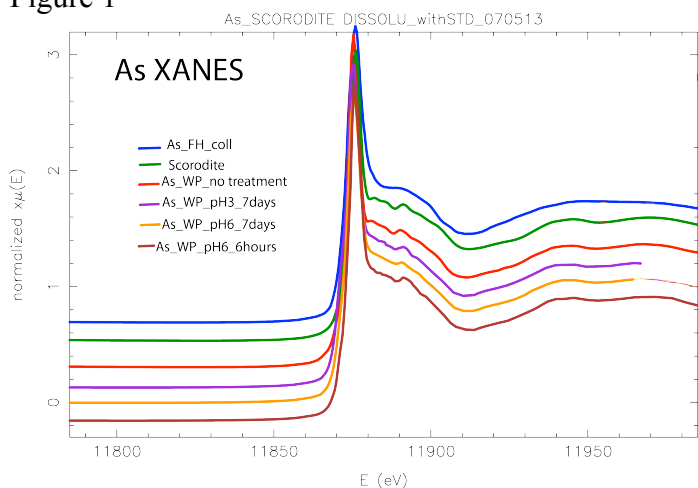
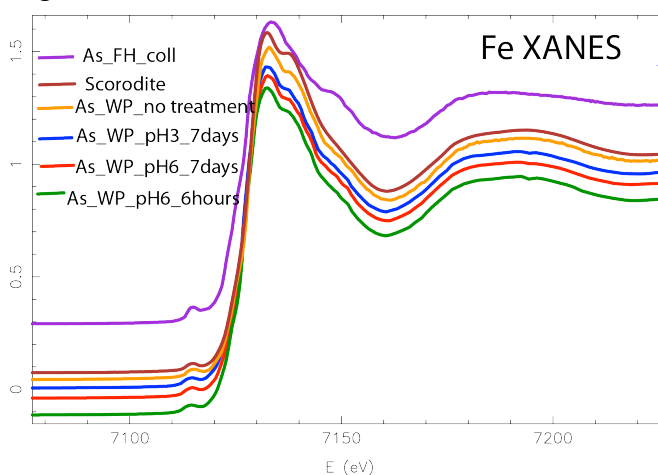


Figure 2



As can be seen in Figures 1 and 2, XAS spectra of the colloidal fractions showed scorodite and As sorbed on ferrihydrite in different proportions as the main components in the colloid samples.

Chemical analysis of the colloid suspensions showed lower As and higher Fe concentration at pH 3 than at pH 6. These results indicate higher scorodite dissolution at pH 6 than at pH 3 and ferrihydrite precipitation at pH 6.

## Conclusions

Colloidal scorodite, present in a waste pile situated in an abandoned smelting factory, partially dissolves depending on pH and agitation time. Higher dissolution occurs at pH 6 than at pH 3, indicating higher scorodite stability at acidic pH than at neutral ones. This is an important information for the remediation of the site and the preservation of the surrounding area from As contamination. In addition, XAS preliminary analyses showed the presence of scorodite and As sorbed in ferrihydrite as the main components of the colloid samples. Higher proportion of ferrihydrite was found at pH 6 corroborating the precipitation of this mineral and its potential role as an As carrier. Further studies will investigate stability and transport processes of colloidal particles within the project CGL2010-17434 supported by the Spanish National Research Plan.

Total results are in preparation as:

M.A. Gómez-González, S. Serrano, F. Laborda, E. Bolea and F. Garrido. Dissolution of colloidal Scorodite as a function of pH and reaction time: role of ferrihydrite as As carrier. *In preparation*