

## 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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

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

Reports can 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> Speciation control in thermochromic cobalt and nickel complexes and their effect on electrodeposition in Deep Eutectic Solvents	<b>Experiment number:</b> CH 5044
<b>Beamline:</b> BM26A	<b>Date of experiment:</b> from: 02.03.2017 to: 06.03.2017	<b>Date of report:</b>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dipanjan Banerjee	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): G. Frisch* (Institut für Anorganische Chemie, TU Bergakademie Freiberg) J. Hartley* (Institut für Anorganische Chemie, TU Bergakademie Freiberg) N. Frenzel* (Institut für Anorganische Chemie, TU Bergakademie Freiberg) R. Harris* (Department of Chemistry, University of Leicester)		

## Report:

EXAFS spectra were acquired for a selection of different arsenic-, copper-, iron- and lead-containing minerals dissolved in either Ethaline or Reline (1:2 molar mixtures of choline chloride, with ethylene glycol or urea, respectively), or in aqueous media for comparison. Spectra of metal foils or solid salts ground and pressed with cellulose powder were used for reference purposes. In general, 4-6 scans were measured, depending on signal and sample concentration.

All samples were measured in both fluorescence and transmission mode. Data for the arsenic samples was very good to  $14 \text{ \AA}^{-1}$ , down to a concentration of 1 mM. We have previously measured samples at the As K-edge at the DUBBLE beamline in 2010 (CH3232) and the data from the current trip is of equal or greater quality than previously. The copper samples could also be measured to  $14 \text{ \AA}^{-1}$ , down to a concentration of 4 mM, whilst the iron samples could be measured to  $12 \text{ \AA}^{-1}$ , with a minimum concentration of 9 mM. An artifact arising from the X-ray optics in the form of a small step in absorbance was observed in all lead spectra above  $10 \text{ \AA}^{-1}$ , however after truncation of the data after 13450 eV, good fits to the first shell could still be obtained.

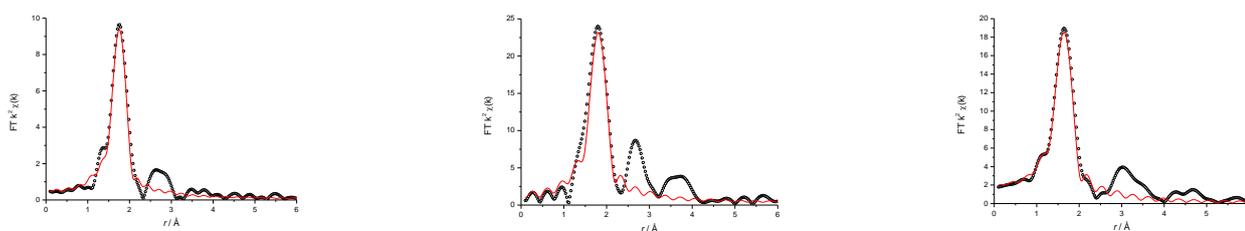
Electrodissolved samples of loellingite and arsenopyrite in Ethaline and Reline were measured at the As K-edge. Speciation changes were observed between the two solvents, but not between the minerals, indicating that the mineral composition has little effect on the solution species formed. In Reline, coordination of As directly to 5-6 urea ligands is

proposed. This is supported by the presence of multiple scattering signal around 3-4 Å. In Ethaline, two peaks are observed that can be fitted to ethylene glycol chelation, whilst identification of the third peak is more complex. It is proposed that it could be multiple scattering of an octahedral complex or a binuclear complex. In both cases, the As-O bond is very short, at 1.7-1.8 Å, with small values for thermal disorder. Compared to a reference solution of As<sub>2</sub>O<sub>3</sub>, the coordination number is significantly larger, indicating that perhaps As(V) has been formed during sample electrodisolution.

Samples measured at the Cu K-edge tended to form Cl-complexes in Ethaline and mixed species in Reline, all with 4-coordination. The main exception to this was the copper(I) telluride mineral, which formed a pure O-donor complex in Ethaline. Metal-ligand distances were calculated to be 2.24 Å for Cu-Cl, and 1.95 Å for Cu-O. As there were no peaks in the 3-4 Å region, it is likely that O-donors could be from absorbed atmospheric moisture or OH-formed during the electrolysis process.

The iron-containing samples tended towards formation of mixed Cl-/O- or pure O-donor complexes in all ionic liquids, except for FeCl<sub>3</sub> in Ethaline, which formed the anticipated tetrachloro complex.

The lead samples in Ethaline displayed multiple peaks, with a first-shell coordination of 2.5xO. These additional peaks could indicate a chelated species, or the presence of a multinuclear complex. The solubility of lead salts in Ethaline is very low, suggesting that the presence of very fine PbO must also be considered. In Reline, 4xCl-coordination was observed. Metal-ligand distances were calculated to be 2.7 Å for Pb-Cl, and 2.3 Å for Pb-O. These findings for lead are contrary to the findings for the other metals studied, where Ethaline tends towards pure Cl-coordination, and Reline tends towards mixed or O-donor coordination.



*Fourier transforms of the EXAFS data (circles) and fits (line) for As<sub>2</sub>O<sub>3</sub> 20 mM in Ethaline (left), and arsenopyrite in Ethaline (middle) and Reline (right). First shell fits only.*

We also attempted to measure the speciation of chalcopyrite in an aqueous chloridic solution, to provide a direct comparison of speciation between DES and aqueous media. Copper tended towards forming a Jahn-Teller distorted octahedral O-donor complex, whilst iron could potentially have the presence of a small amount (1xCl max.) of Cl in the coordination sphere. This behaviour reflects the aqueous coordination chemistry of these elements.

These results have allowed us to determine how the speciation of four different metals changes when electrodisolved from different sulphide minerals. It was observed that the first coordination shell commonly contained a higher proportion of O-donors when the sample was prepared via electrolysis.