



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.



Experiment title: Structure of Cu(I) chloro-complexes in hypersaline solutions		Experiment number: ME-998
Beamline: BM-01B	Date of experiment: from: 6 July 2005 to: 11 July 2005	Date of report:
Shifts: 12	Local contact(s): Hermann Emerich	<i>Received at ESRF:</i>
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Report:

Introduction: The transport of metals in hypersaline brines over a wide range of temperatures played a fundamental role in the formation of most Cu, Au, Pb, Zn, Ag and U ore deposits. In addition, hypersaline brines form a significant proportion of present-day surface water in semi-arid environments, and hence understanding metal transport in hypersaline brines is important to predict the dispersion of contaminants around ore deposits (geochemical prospecting) and waste deposits. Despite this, the nature and stability of the aqueous complexes of trace metals in hypersaline brines is poorly understood.

A number of recent studies have been devoted to Cu(I) chlorocomplexes from room temperature to 325°C, using a variety of techniques: solubility experiments [1,2], UV-Vis spectrophotometry [3], and EXAFS [4]. The latter experiments show that linear $\text{CuCl}(\text{H}_2\text{O})(\text{aq})$ and CuCl_2^- exist in moderately saline solutions (≤ 2 m) up to 325°C. However, [3] observed the appearance of two further Cu(I) chlorocomplexes at higher salt concentrations. Based on the shape of the absorbance spectrum of these species, they suggested that tetrahedral $\text{Cu}(\text{OH})_2\text{Cl}_3^{2-}$ and CuCl_4^{3-} are the dominant species at high salt concentrations.

The aims of this experiment were to:

- Test a titanium hydrothermal cell for EXAFS collection at elevated P-T.
- Investigate the speciation of Cu(I) in highly concentrated chloride solutions.
- Check that the assumptions used by [3] for interpreting UV-Vis data (i.e., that the Beer-Lambert law was valid over the large range of salinity) were valid.
- Obtain an integrated speciation model that can explain all available evidence (UV-Vis, solubility, EXAFS, preliminary XANES experiments conducted at the Photon Factory).

Experimental: Fluorescence Copper (8979 eV) *K*-edge XANES and EXAFS spectra of Cu(I) in acidic chloride solution containing up to 17 m LiCl were measured in fluorescence mode at 150°C using a titanium (grade 2) pressure cell equipped with kapton windows. The cell was placed in a cylindrical aluminum block hosting two cartridge heaters. The temperature was controlled to a precision of $\pm 1^\circ\text{C}$. Some standard solutions and minerals were measured at room temperature. Powdered minerals were pressed into pellets (13 mm radius, ~ 2 mm thickness) diluted with BN. The solutions for room temperature

measurements were placed into Teflon solution cells equipped with Kapton windows. The cell to fluorescence detector distance was varied with changing solution concentration, to optimise the counts. The synchrotron was operating in uniform bunch mode with a maximum current of 200 mA.

The solutions were prepared carefully under oxygen-free conditions, and a small quantity of metallic copper was loaded in the cell to reduce traces of Cu(II) that may occur in solution. We found that the reduction of Cu(II) was very rapid; indeed, as Figure 1 shows, even a sample consisting predominantly of Cu(II) (XANES spectrum with no pre-edge feature, and a broad band at 8998 eV) reduces completely at 150°C in less than an hour.

Results: As the chloride concentration is increased from 1.5 to 17 molal, XANES data (Figure 2) show first a decrease in the peak height in pre-edge region, (1.5 to 8 m) and then an increase in intensity as well as a slight shift in edge position towards higher energy. These changes are consistent with a change in the complex geometry from linear (CuCl_2^-) to trigonal planar (CuCl_3^{2-}) to tetrahedral (CuCl_4^{3-}) [5]. The interpretation in terms of these three complexes is also supported by principal component analysis on the XANES and EXAFS data.

We tested for potential artefacts resulting from self absorption using the FLUO self absorption correction routine that is incorporated in ATHENA. Self absorption effects were negligible, even for the solutions containing the highest Cu concentration.

Conclusions:

- The titanium hydrothermal cell for EXAFS collection worked as expected at 150°C. Transmission spectra could be collected for the most dilute samples.
- A speciation model including linear CuCl_2^- , a new trigonal planar complex CuCl_3^{2-} and a tetrahedral CuCl_4^{3-} is consistent with available solubility, UV-Vis, and EXAFS data.
- The XANES data strongly support the assumption of validity of the Beer-Lambert law for hypersaline solutions.
- XANES is a powerful tool in this example to decipher complex speciation with multiple geometry changes. The quantitative interpretation of the EXAFS data is on-going.

Figure 1: Heating Cu in 1.5 m LiCl from 70 to 150 °C

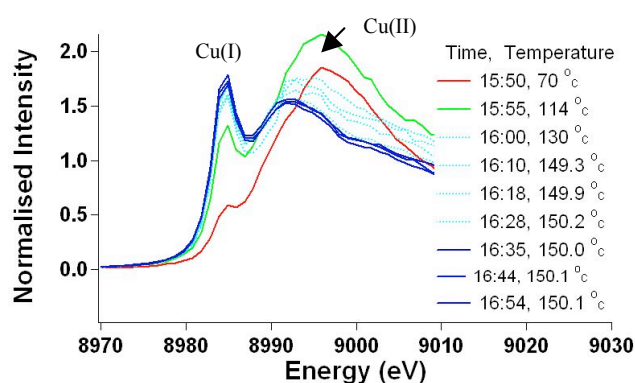
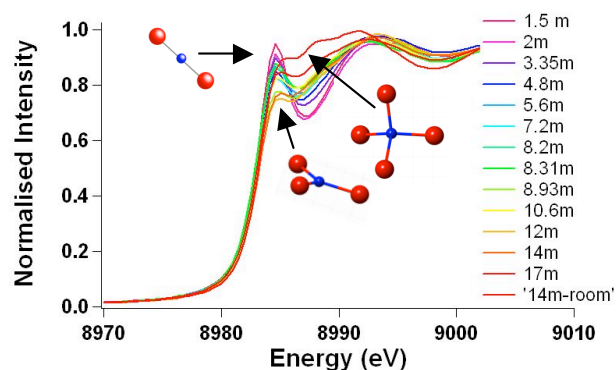


Figure 2: XANES spectra of Cu(I) in 1.5 to 17 m LiCl



References

1. Xiao, Z.; Gammons, C.; Williams-Jones, A. *Geochimica et Cosmochimica Acta*, **1998**, 62, 2949.
2. Liu, W.; McPhail, D. C.; Brugger, J. *Geochimica et Cosmochimica Acta* **2001**, 65, 2937.
3. Liu, W.; Brugger, J.; McPhail, D. C.; Spiccia, L. *Geochimica et Cosmochimica Acta* **2002**, 66, 3615.
4. Fulton, J. L.; Hoffmann, M.; Darab, J. G.; Palmer, B. J.; Stern, E. A. *Journal of Physical Chemistry* **2000**, 104, 11651.
5. Kau, L.; Spira-Solomon, D.; Penner-Hahn, J. E.; Hodgson, K. O.; Solomon, E. I. *Journal of the American Chemical Society* **1987**, 109, 6433.