

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: XAS study of octahedral-tetrahedral transition of cobalt chloride complexes in hydrothermal brines	Experiment number: 3002943
Beamline: BM30B	Date of experiment: from: 01 July, 2009 to: 08 July, 2009	Date of report: 28/08/09
Shifts:	Local contact(s): Denis Testemale	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

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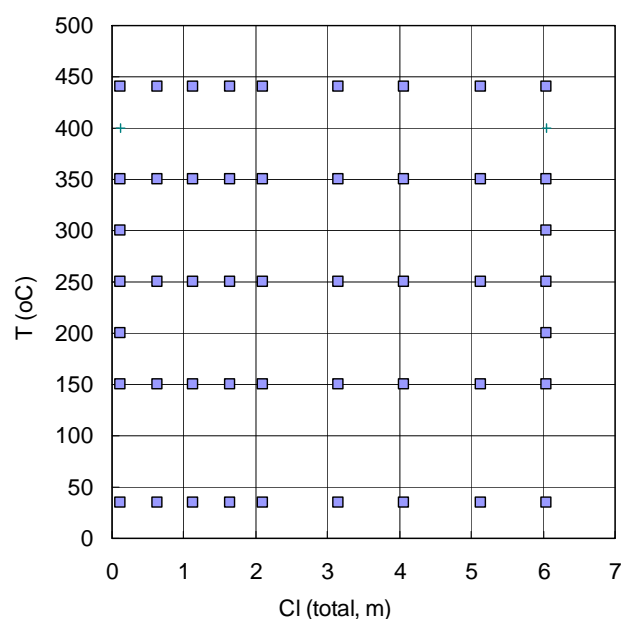
Joel Brugger*, Adelaide University, Australia

Report:

Synchrotron XAS measurements at the cobalt *k*-edge for Co bearing chloride solutions have been successfully conducted at the FAME beamline (BM30B) at ESRF on 1-8 July 2009. The aim of this project was to i) determine the structure (coordination numbers and distances) of Co(II) chloride complexes at temperatures up to 500 °C at 600 bar, as a function of varying Co/Cl ratios, and ii) derive the formation constants for aqueous Co(II) chloride complexes.

Operations at the facility were incident free, and setup and data collection were performed without any significant issues. Cobalt *k*-edge EXAFS spectra were collected with sodium chloride concentration ranging from 0 to 6 molal and temperature range from 35 °C to 440 °C (Table 1). XAS data have also been collected for CoBr₂ in water and 6 m NaBr solution at the same pressure over the same temperature range.

Table 1 Temperature and NaCl concentration ranges for XAS measurement. Two to five spectra were collected at each point .



At room temperature (35 °C), the XANES spectra do not change noticeably with increasing chloride concentration, indicating the coordination structure of the predominant cobalt species remain the same. With increasing temperature, however, the XANES spectra show systematic changes:

1). For solutions with 57 mmol CoCl₂ and added NaCl, the change of the XANES spectra indicates the possible octahedral (Co(H₂O)₆²⁺) to tetrahedral (CoCl₄²⁻) transition. The XANES spectra with increasing temperature for 6 m NaCl solution are shown in Figure 1.

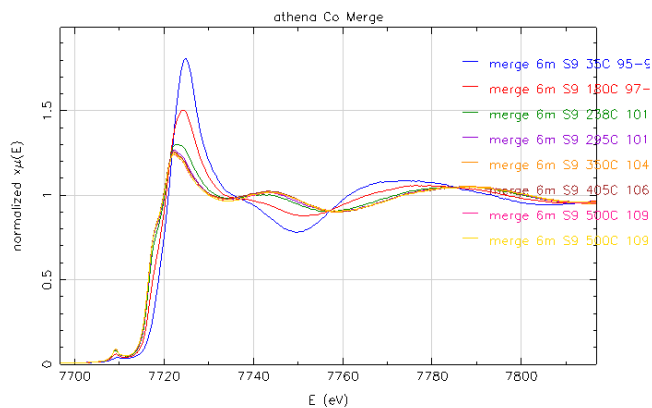


Figure 1 XANES spectra for 57 mmol CoCl₂ in 6 m NaCl solution at 35 to 440 °C.

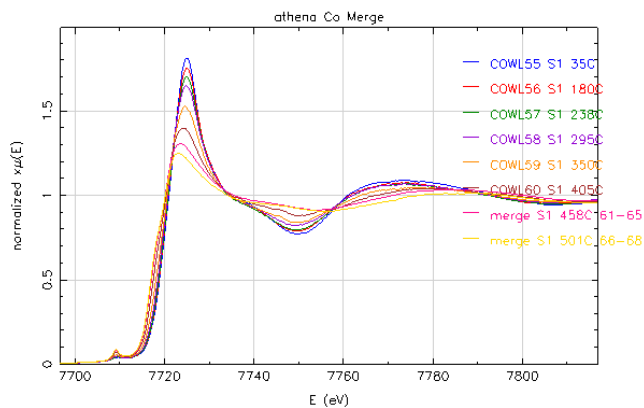


Figure 2 XANES spectra for 57 mmol CoCl₂ solution at 35 to 440 °C

2) For 57 mmol CoCl₂ solution without added NaCl, the change of the XANES with increasing temperature is different (Figure 2). This may indicate that the species predominating in this solution at 440 °C is probably tetrahedral with mixed Cl and O ligands (e.g., CoCl₂(H₂O)₂), since the Co:Cl ratio is 2 for this solution. The difference between the two XANES spectra at 440 °C is shown in Figure 3. EXAFS data analysis will reveal their bond distance, coordination numbers and ligand identities.

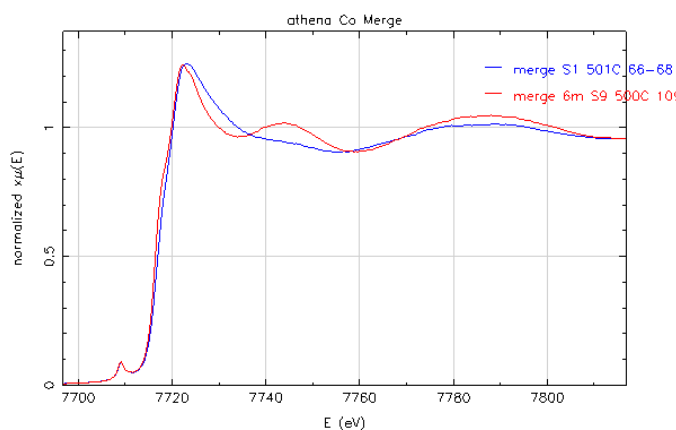


Figure 3 Comparison of two XANES spectra of Co solutions at 440 °C. Blue line represents no added NaCl, and the red line a 6 m NaCl solution. Note that they both have a distinctive pre-edge

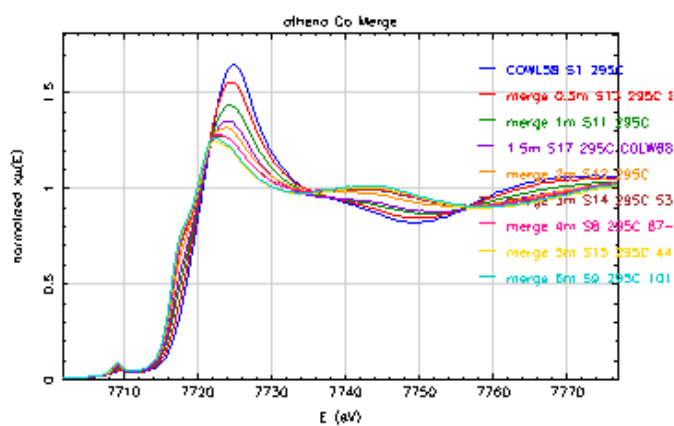


Figure 4 XANES spectra of Co solutions with 0-6 m NaCl at 250 °C.

3) The evolution of the XANES spectra with increasing chloride concentration at a given temperature are best shown using the 295 °C data as an example (Figure 6). The pre-edge 1s-3d transition peak at 7709 eV increases with increasing chloride concentration (Figure 6b), indicating an increase of the tetrahedral species.

In summary, the XAS data we collected are of high quality and show systematic changes as a function of temperature and chloride concentration. The EXAFS data analysis, ab initio XANES calculation and thermodynamic regression are in progress and will reveal a full picture of cobalt speciation in chloride solutions over a wide range of salinity and temperature (0-6 mol and 35-440°C at 600 bar).