EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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://wwws.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.

ESRF	**Experiment title:** A novel view on the extraction mechanism of metals by anion exchangers	**Experiment number**: 26-01-1120
Beamline:	**Date of experiment**: from: 08/09/2017 to: 11/09/2017	**Date of report**:
Shifts: 12	**Local contact(s)**: Dipanjan Banerjee	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Tom Vander Hoogerstraete*, Nagaphani Kumar Batchu, Zheng Li, Michiel Van de Voorde

KU Leuven - University of Leuven

Department of Chemistry

Laboratory of Inorganic Chemistry

Celestijnenlaan 200 F bus 2404

B-3001 Heverlee (Belgium)

Report:

Our beamtime at the DUBBLE beamline has been again very succesful. In addition the the planned experiments, written in the proposal, we had even time for other measurements as well. We hope to publish the results in 4 or 5 different articles in the next years. We were also very happy with the support of the beamline scientist, especially during weekend (out of the working hours)

The speciation of the following metals in a solution containing 0 to 12 M HCl have been studied: Sb, Cu, Ga, Co and Nb.

Figure 1 shows the fourier transforms of the EXAFS functions from 0 to 12 M for copper. A shift in the fourier transform of the EXAFS function can be seen from 0 to 12 M HCl. At 0 M HCl, copper is coordinated by 4+2 (jahn teller effect) oxygens atoms. With an increasing chloride concentration, the oxygen atoms are replaced by chloride atoms

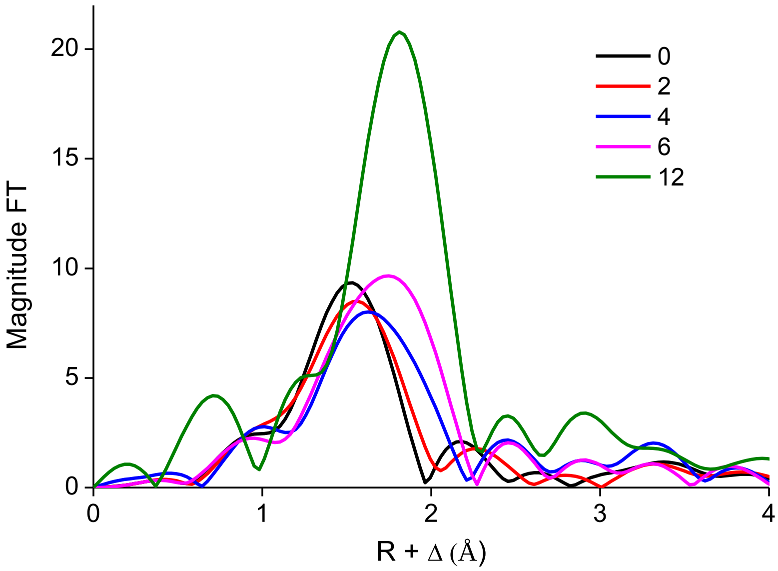

Figure 1. Fourier transform of the EXAFS function of Cu(II) at different HCl concentrations.

Further more detailed analysis, similar to what we have done recently on indium, [1] is required to determine the number of oxygens and chlorines in the first coordination shell of all metals studied.

In addition, we could study the oxidation and reduction of Eu(II) in nitrate media as a function of time and media. Therefore, we have measured a lof of XANES spectra. One of these measurements is shown in Figure 2.

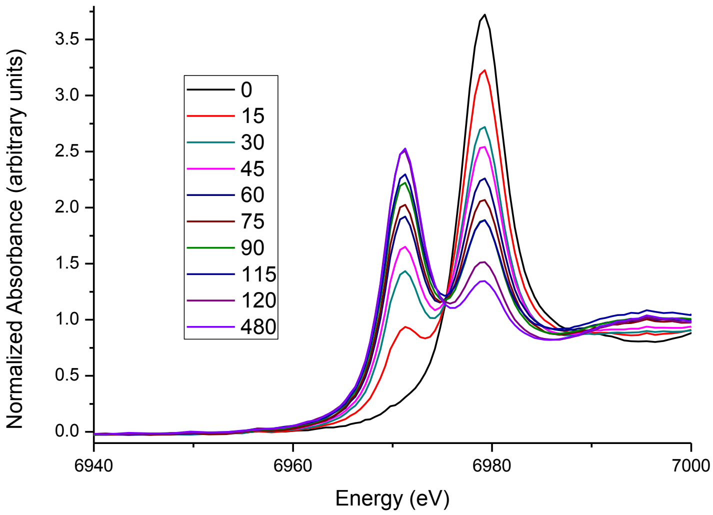

Figure 2. Absorption edge of Eu(III) as a function of time after reduction with Zn(0) powder.

Lastly, we were able to measure and model several EXAFS functions of complexes formed in deep eutectic solvents and ionic liquids (table 1 and table 2)

Table 1. First row transition metal complexes formed in a mixture of 0.6/99.4 wt% or 15/85 wt% water/deep eutectic solvent mixtures. The data are obtained by EXAFS analysis.

Medium	complex	N	R (Å)	Debye Waller (Å^2)
15% H2O	$Ni(H_2O)_6^{2+}$	5.8(1)	2.051(1)	0.007(1)
15% H2O	$ZnCl_4^{2-}$	3.9(1)	2.262(2)	0.008(1)
15% H2O	$CuCl_2^-$	2.5(1)	2.038(1)	0.003(1)
0.6% H2O	$NiCl_4^{2-}$	4.3(1)	2.212(1)	0.011(1)
0.6% H2O	$CuCl_2^-$	2.2(1)	2.026(1)	0.004(1)

Table 2. Complexes formed after leaching the metallic form of the metal with the ionic liquid $P_{66614}Cl_3$. The data are obtained by EXAFS analysis.

Metal oxidation state	Complex formed	N	R (Å)	Debye Waller (Å^2)
Fe(III)	$[FeCl_4]^-$	4.4(2)	2.208(2)	0.004(1)
Cu(II)	$[CuCl_4]^{2-}$	4.0(1)	2.244(1)	0.007(1)
Zn(II)	$[ZnCl_4]^{2-}$	3.9(1)	2.304(2)	0.006(1)
Ga(III)	$[GaCl_4]^-$	4.6(1)	2.184(1)	0.004(1)
In(III)	$[InCl4]^-$	3.7(2)	2.365(3)	0.004(1)

[1] C. Deferm, B. Onghena, T. Vander Hoogerstraete, D. Banerjee, J. Luyten, H. Oosterhof, J. Fransaer, K. Binnemans, Speciation of indium(III) chloro complexes in the solvent extraction process from chloride aqueous solutions to ionic liquids, Dalton Trans. 46 (2017) 4412–4421. doi:10.1039/C7DT00618G.