EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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:** Studying the disproportionation of biogenic elemental selenium nanoparticles (BioSeNPs) during their interaction with Cu(II)	**Experiment number**: 26-01-1069
Beamline:	**Date of experiment**: from: 24th June, 2016 to: 28th June, 2016	**Date of report**: 22nd Aug, 2016
Shifts: **12**	**Local contact(s)**: Dr. Dipanjan Banerjee	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Rohan Jain[a], Eric D van Hullebusch[b]*, Francois Farges[c], Piet Lens[a,d]

a) Tampere University of Technology, Tampere, Finland

b) Université Paris-Est, Laboratoire Géomatériaux et Environnement (EA 4508), UPEM, Marne-la-Vallée, France

c) Laboratoire de Minéralogie et de Cosmochimie du Muséum, Muséum National d'Histoire Naturelle, 75005 Paris, France

d) UNESCO-IHE, Delft, The Netherlands

Report:

A) Overview:

Elemental Se is known to disproportionate into selenite and selenide in the presence of heavy metals such Cu.[1] The formed selenide would react to form metal selenide nanoparticles[1]. Both metal selenide and selenite are bioavailable and also more toxic than elemental selenium even at as low concentration as 10 μg L^{-1}.[2] Indeed, CuSe formation has been reported after interaction of chemogenic Se NP with Cu, however, neither the direct experimental evidences nor the mechanism of formation was described (disproportionation of Se or redox reaction of Cu(I) and Se).[3] The simultaneous presence of biogenic elemental selenium nanoparticles (BioSeNPs) and Cu in engineered systems (e.g. bioreactors treating selenium containing wastewater) and natural systems (sediments) can potentially lead to the formation of toxic by-products (metal selenide and selenite). However, there is so far no study to evaluate the disproportionation of BioSeNPs. This study is further complicated by the fact that BioSeNPs can adsorb Cu onto their surface. The adsorbed Cu are known interact with hydroxyl and carboxyl groups present on the surface of BioSeNPs that are capped with extracellular polymeric substances.[4,5] Both infrared and X-ray photoelectron spectroscopy cannot distinguish between the electrostatic and covalent bond between BioSeNPs and Cu. X-ray Absorption Spectroscopy (XAS) is only technique to experimentally confirm the formation of CuSe and disproportionation of BioSeNPs.

B) Data quality:

The measurements were successful and data recorded was of high quality. A variety of model compounds (those which were not measured during earlier experiments) and samples were measured at Cu-k edge. As the Cu concentration was high enough in the sample, we were able to record the data successfully, thanks to the Ge-solid state detector. Moreover, the cryostat has helped to measure the data at 30 K, thus improving a lot in the data quality. To this end, we would like to acknowledge the help from Dr. Dipanjan Banerjee for his valuable support through out the beam time.

C) Status and progress of evaluation:

Primary data reduction has already been carried out. More detailed analysis including shell by shell fitting will be carried out in the following months. The primary data analysis suggests to some interesting findings (please see section D for more details) and excellent signal/noise ratio related to excellent beam stability and detector sensitivity.

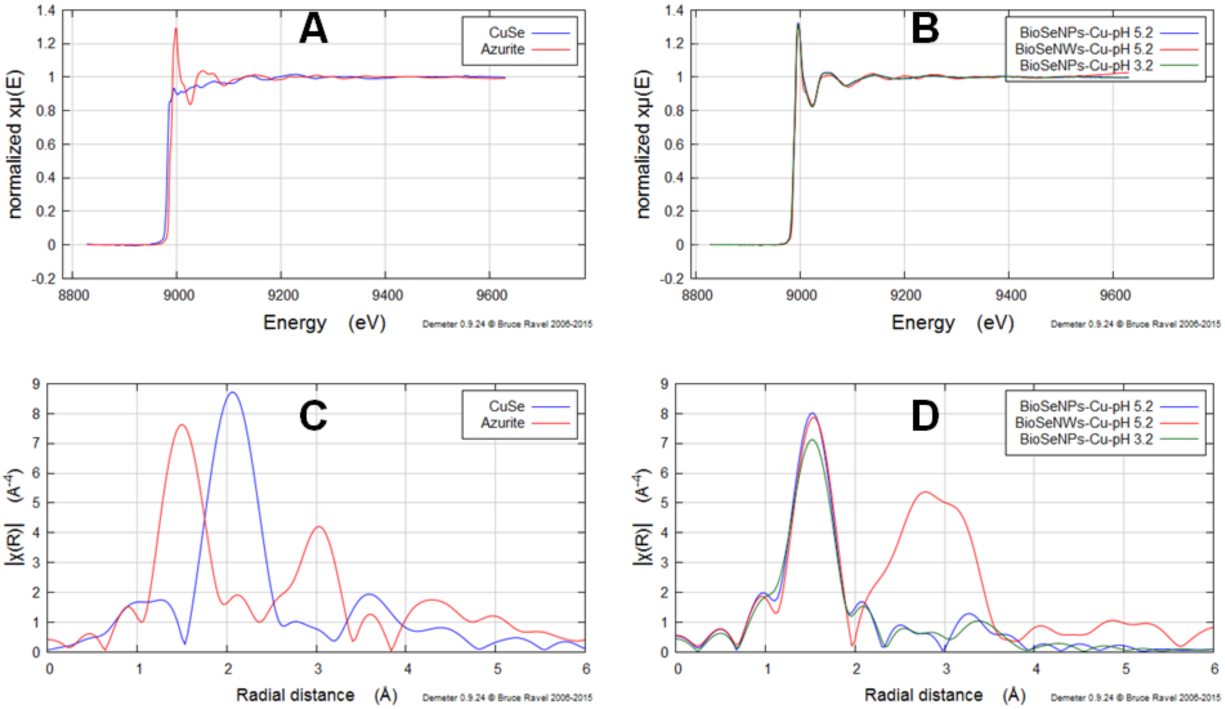

Figure 1. Cu K-edge data collected for (A) model compound and (B) for different samples. k^3 weighted fourier transformation of the (C) model compounds and (D) samples. The model compounds data were collected in transmission mode while that of samples were collected in fluorescent mode at 30 K. Please note that BioSeNPs and BioSeNWs, respectively, refers to biogenic elemental selenium nanoparticles and biogenic elemental selenium nanowires.

D) Results:

The primary data analysis already suggests different mechanisms of Cu adsorption onto amorphous biogenic elemental selenium nanoparticles (BioSeNPs) and trigonal biogenic elemental selenium nanowires (BioSeNWs). It is also interesting that the presence of CuSe or Cu$_2$Se was apparently absent in the samples.The results obtained at DUBBLE indicates the interaction of Cu is primarily to the polymeric substances attached to the surface of BioSeNPs. The preliminary analysis also suggest the presence of Cu(OH)$_2$ which is reasonable as the equilibrium pH was around 6.2 that would lead to the precipitation of the Cu. It seems that Cu is present in the polyhedra CuO$_6$ or CuO$_4$+1+1 due to Jahn-teller effect which would reduce the symmetry and energy. This understanding would help us to more closely predict the fate of BioSeNPs in the environment.

References:

1. Li, Y., Ding, Y., Liao, H. & Qian, Y. Room-temperature conversion route to nanocrystalline mercury chalcogenides HgE (E=S,Se,Te). *J. Phys. Chem. Solids* **60,** 965–968 (1999).
2. Lenz, M. & Lens, P. N. L. The essential toxin: the changing perception of selenium in environmental sciences. *Sci. Total Environ.* **407,** 3620–33 (2009).
3. Bai, Y. *et al.* Removal of copper from aqueous solution by adsorption on elemental selenium nanoparticles. *J. Chem. Eng. Data* **56,** 2563–2568 (2011).
4. Jain, R. *et al.* Extracellular Polymeric Substances Govern the Surface Charge of Biogenic Elemental Selenium Nanoparticles. *Environ. Sci. Technol.* **49,** 1713–1720 (2015).
5. Jain, R. *et al.* Preferential adsorption of Cu in a multi-metal mixture onto biogenic elemental selenium nanoparticles. *Chem. Eng. J.* **284,** 917–925 (2016).