

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.



	Experiment title: Effect of Ozonation on Speciation of Cu, Zn, and Cd in Wastewater Effluent	Experiment number: 01-01-1003
Beamline: BM26A	Date of experiment: from: 22.09.2016 to: 27.09.2016	Date of report:
Shifts:	Local contact(s): Dipanjan Banerjee (email: banerjee@esrf.fr)	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Dr. Ralf Kaegi Basilius Thalmann Dr. Andreas Voegelin		

Report:

The aim of the proposal was to investigate the oxidation kinetics of CuS, ZnS and CdS during reaction with ozone as well as the speciation of Cu, Zn and Cd in wastewater effluent after ozonation.

Qualitative comparison of experimental XANES spectra of effluent water that was treated with ozone suggested that Zn was primarily sorbed to iron(hydr)oxides, and Cu was probably complexed to organic material. Due to the low Zn and Cu concentrations in the effluent water, the spectra however were of limited quality and could not be investigated in more detail. We therefore decided to investigate the transformation of CuO and ZnO-NP reacted with bisulfide (HS^-) over time instead. The compiled results from the CuO NP study are summarized in a manuscript that will be submitted to Environmental Science Nano shortly. A brief summary of the background and the results of the measurements performed at ESRF is provided below.

Background

In addition to their use in the fields of catalysis, electronics and energy, copper oxide nanoparticles (CuO NPs) are increasingly used in a variety of biocide applications, such as wood preservation, anti-fouling coatings and agricultural pesticides (Kiaune and Singhasemanon 2011). CuO NPs from these specific applications and ZnO-NP mainly from personal care products may be released to the wastewater stream and transported to a wastewater treatment plant (WWTP). The sulfidation of chalcophile elements, such as Cu and Zn, favored by the elevated concentration of bisulfide (HS^-) in wastewater systems (Liu, Pennell et al. 2011), will strongly influence the speciation and the bioavailability of these elements in (treated) wastewater and in the sewage sludge. In previous studies, only the endpoints of the reaction were investigated, leaving the reaction kinetics and mechanisms largely unexplored. For an exposure assessment of biota to CuO/ZnO NP, however, the transformation rates of these NP in different (waste)water systems are essential and have to be related to typical residence times in the respective systems. In this study, we, therefore, investigated the sulfidation of CuO- and ZnO-NP, in the presence of HS^- in aerated solutions buffered to pH 8.

Experimental procedures and results

Based on prior knowledge derived from TEM analyses and laboratory experiments to assess the sulfidation rates of CuO, we conducted additional time-resolved CuO-NP sulfidation experiments designed to enable the analysis of the solid phase by XAS. CuO NP (1.3 mM, 50 nm) were reacted with HS⁻ (4.2 mM) for up to 2 days. At selected time points, samples were collected by directly pipetting the reacting suspensions into liquid nitrogen cooled samples holders. The reaction progress monitored by determining the speciation of Cu using Cu K-edge XAS. The recorded XANES spectra and the corresponding LCF results are given in Figure 1 and 2A, respectively. XANES spectra showed a steady decrease of an oscillation at 8997 eV (Figure 1, dashed line), a typical feature of CuO. The spectra became considerably flatter during the first 15 minutes and strongly resembled the spectrum of amorphous Cu_xS. Over time, a shoulder gradually appeared at 8985 eV (Figure 1, dotted line), which is characteristic for crystalline CuS (covellite). After 3 d the experimental spectrum was very similar to the reference spectrum of covellite. The evolution of the XANES spectra thus suggests an initial transformation of CuO to amorphous Cu_xS and ultimately to covellite, consistent with XAS results of Patrick et al. (1997) for the reaction of dissolved Cu²⁺ with bisulfide. LCF analysis of the XANES spectra supported the qualitative interpretation of the spectral sequence (Figure 1A). The XAS-based results are supported and complemented by TEM images revealing distinct morphological and chemical changes of the nanoparticles over time (Figure 2B): Aggregates of ~40 nm CuO primary particles, representing the crystalline starting material, initially transformed into Cu_xS particles of comparable size but with a fuzzy internal structure (HAADF), reflecting the fast conversion of crystalline CuO into amorphous Cu_xS (Figure 2B at 5 min). The comparable size of the pristine and transformed primary particles and the similar morphology of their aggregates suggests that this transformation occurred via a direct solid-fluid reaction mechanism.

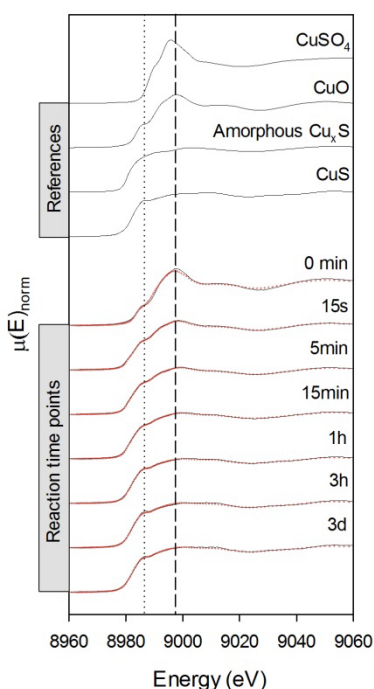


Figure 1: Normalized XANES spectra of the references used for the LCF analysis and experimental spectra collected at increasing reaction times (solid black lines). The reference spectrum of amorphous Cu_xS was obtained from Patrick et al. (1997). The red dots represent the reconstructed LCF spectra.

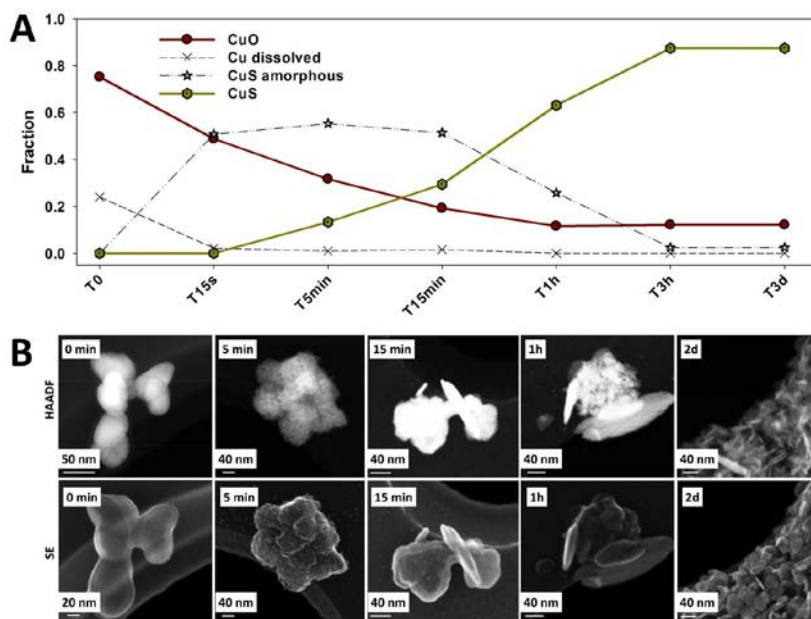


Figure 2: (A) Changes in Cu speciation over time as determined by LCF analysis of the XANES spectra (shown in Fig. 1). (B) STEM – HAADF (upper panel) and SE (lower panel) micrographs showing agglomerated particles at selected time points (1.3 mM CuO, 4-fold excess of HS⁻). The micrographs for 0 min represent the unreacted CuO-NP.

In a second set of time-resolved experiments, ZnO NP (1.2 mM, 50nm) were reacted with HS⁻ (11.1 mM) in the absence or presence of 10, 100 and 1000 ppm humic acid for up to 10 days and the reaction progress was monitored by determining the Zn speciation using Zn K-edge XAS (Figure 3 A and B). The sulfidation occurred in two distinct phases: a very fast initial reaction of ZnO to ZnS was followed by a much slower reaction, which was complete after 10 days (Figure 3A). In the presence of HA higher reaction rates were observed (Figure 3B). TEM analyses indicated the formation of core-shell structures which developed into hollow ZnS spheres over time. (Figure 3C and D)

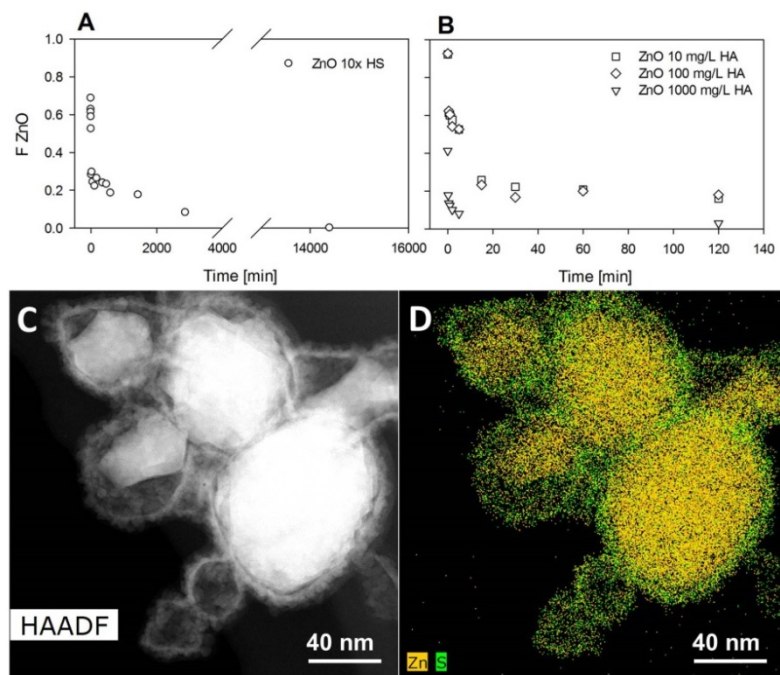


Figure 3: (A) Fraction of ZnO determined at different time points of the reaction with a HS⁻:Zn ratio of 10 using linear combination fit analysis performed on XANES spectra. (B) Fraction of ZnO determined at different time points of the reaction with 10x excess HS⁻ in the presence of 10, 100 and 1000 mg/L HA. (C) STEM-HAADF image of ZnO NP after 4 d reaction at 1.2 mM and a HS⁻:Zn ratio of 5. (D) Corresponding EDX elemental mapping. Zn signals are shown in yellow and S signals in green.

Environmental implications

Experimentally determined sulfidation half-life times were between a few seconds and several minutes and typical hydraulic residence times in wastewater systems range from 24 h up to several days. Thus, CuO NP will be completely sulfidized in wastewater systems. LCF analyses of XAS spectra revealed much higher sulfidation rates of ZnO-NP in the presence of HA, in agreement with previous results reported for the sulfidation of silver-NP. (Thalmann, Voegelin et al. 2016). The XAS data acquired in this study complemented by TEM analyses revealed different sulfidation rates and mechanisms for CuO- and ZnO-NP, which have to be taken into consideration when assessing the impact of these NP on environmental and engineered systems.

References

- Kiaune, L. and N. Singhasemanon (2011). Pesticidal copper (I) oxide: environmental fate and aquatic toxicity. *Reviews of Environmental Contamination and Toxicology Volume 213*, Springer: 1-26.
- Liu, J., K. G. Pennell and R. H. Hurt (2011). "Kinetics and mechanisms of nanosilver oxysulfidation." *Environmental science & technology* **45**(17): 7345-7353.
- Patrick, R., J. Mosselmans, J. Charnock, K. England, G. Helz, C. Garner and D. Vaughan (1997). "The structure of amorphous copper sulfide precipitates: An X-ray absorption study." *Geochimica et Cosmochimica Acta* **61**(10): 2023-2036.
- Thalmann, B., A. Voegelin, E. Morgenroth and R. Kaegi (2016). "Effect of humic acid on the kinetics of silver nanoparticle sulfidation." *Environmental Science: Nano* **3**(1): 203-212.