Experiment Report Form

The double page inside this form is to be filled in for each experiment at the Rossendorf Beamline (ROBL). This double-page report will be reduced to a one page, A4 format, to be published in the Bi-Annual Report of the beamline. The report may also be published on the Web-pages of the FZD. If necessary, you may ask for an appropriate delay between report submission and publication.

Should you wish to make more general comments on the experiment, enclose these on a separate sheet, and send both the Report and comments to the ROBL team.

Published papers

All users must give proper credit to ROBL staff members and the ESRF facilities used for achieving the results being published. Further, users are obliged to send to ROBL the complete reference and abstract of papers published in peer-reviewed media.

Deadlines for submission of Experimental Report

Reports shall be submitted not later than 6 month after the experiment.

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 / experiment 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.
- bear in mind that the double-page report will be reduced to 71% of its original size, A4 format. A type-face such as ”Times” or ”Arial” , 14 points, with a 1.5 line spacing between lines for the text produces a report which can be read easily.

Note that requests for further beam time must always be accompanied by a report on previous measurements.

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ROBL-CRG	**Experiment title:** **Immobilisation of selenite onto Fe_3O_4 , Fe/Fe_3C nanoparticles and mesoporous silica**	**Experiment number**: 20-01-658
Beamline: BM 20	**Date of experiment**: from: 10/04/07 to: 02/10/07	**Date of report**: 28/03/08
Shifts: **12**	**Local contact(s)**: A. Scheinost	*Received at ROBL:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

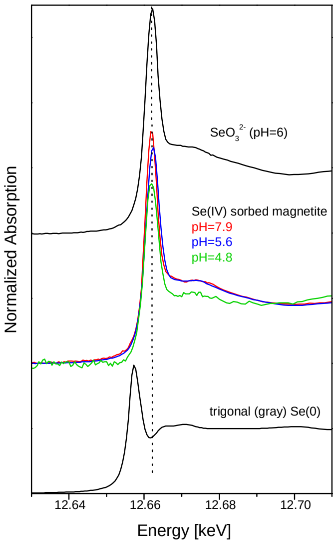
Abstract. During this experiment, we performed XAS speciation of selenite sorbed onto Fe_3O_4 and Fe/Fe_3C nanoparticles (NPs). Fe_3O_4 NPs (d=4-6 nm) have been prepared by co-precipitation of Fe(II) and Fe(III) in basic solutions under ultrasound. Air-stable Fe/Fe_3C NPs (d=25-100 nm) have been prepared by $Fe(CO)_5$ sonicating in diphenylmethane solutions and subsequently annealing the as-prepared product at 700°C in pure argon. Also the preliminary data were obtained on the preparation of zero-valent selenium NPs inserted within the mesoporous silica using power ultrasound. The results on selenite immobilization has been published in ***Environ. Sci. Technol.***

Arroyabe Loyo R.L., Nikitenko S.I., Scheinost, A.C., Simonoff, M. Immobilisation of Selenite on Fe_3O_4 and Fe/Fe_3C Ultrasmall Particles, *Environ. Sci. Technol.*, **2008**, *42*, p.2451.

Immobilization of selenite onto Fe_3O_4 and Fe/Fe_3C NPs:

Figure 1 shows the XANES spectra at selenium *K*-edge for Se(IV) adsorbed onto Fe_3O_4 NPs at different pH values. The strong similarity of the edges in these spectra with that of aqueous selenite indicates that the oxidation state of Se(IV) did not change due to the sorption in the pH range of 4.8–8.0. The selenium k^3-weighted EXAFS signal of the sorption sample at pH 7.9 shows a single sine-like oscillation, corresponding to a backscattering shell at a distance of 1.4 Å before correcting for the phase shift. This shell could be fitted by three O atoms at a distance of 1.70 Å, in line with the structure of Se(IV) compounds. After reduction to Se(0) or Se(−II), one would observe a significant shift of the coordination shell to longer distances, since Se and Fe coordination shells in a variety of solids vary between 2.3 to 2.6 Å. Since no significant backscattering contribution in this range could be found, this is clear evidence that no reduction of Se(IV) took place. The same conclusion applies for the EXAFS spectra at pH 5.6 and 4.8.

In contrast to Fe_3O_4, sorption of Se(IV) onto Fe/Fe_3C NPs causes significant changing in the selenium oxidation state (Figure 2). The XANES absorption edge (12654.8 eV) is 5.5 eV lower than that of aqueous selenite, 1.3 eV lower than that of trigonal Se(0), and similar to that of FeSe (12655.2 eV). At the same time, the white line is reduced in intensity in comparison to Se(IV), suggesting an increased population of the valence 4p levels. Both features are in line with a complete reduction to Se(−II). Thus it can be concluded that the removal of selenite ions with Fe/Fe_3C NPs at anaerobic conditions occurs via Se(IV) reduction to Se(−II). The EXAFS spectrum and the corresponding Fourier transform of the Fe/Fe_3C NPs sample are more similar to those of FeSe than to those of Se(0) and $FeSe_2$. A multishell fit of the spectrum achieved the following structural data: 3.3 Fe @ 2.42 Å, 1.8 Se @ 3.46 Å, and 3.6 Se @ 3.98 Å, which are different from those of tetragonal FeSe: 4 Fe @ 2.37 Å, 8 Se @ 3.77 Å, and 4 Se @ 3.91 Å. The relatively small coordination numbers suggest formation of ultrasmall FeSe particles with a structure somewhat different from that of bulk crystalline FeSe.



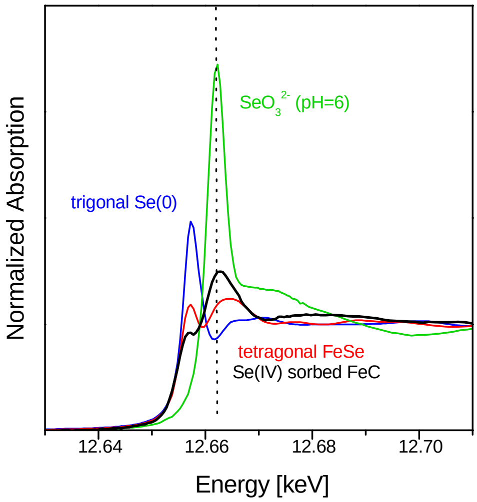


Fig. 1. Se K-edge XANES spectra of Se sorbed at Fe_3O_4 NPs.

Fig. 2. Se K-edge XANES spectra of Se sorbed at Fe/Fe_3C NPs.

Preliminary XAS study revealed formation of a red form of Se(0) NPs after Se(IV) reduction with hydrazine at pH=3.0 in the presence of mesoporous silica SBA-15 under the effect of power ultrasound (I= 30 W/cm^2, f= 20 kHz, T= 36°C, Ar). MET images show that Se(0) NPs are embedded within the mesopores of SBA-15.