DUBBLE – EXPERIMENT REPORT

We kindly request you to answer the questions (max 2 pages) and return the form to NWO **within 2 months of the completion of the experiment** to **dubble@nwo.nl**

Beam time number: 26-01-1016		**Title:** Interaction of selenite and selenate with Boom Clay material: can both forms of selenium be reduced and what are the products?
Beamline: **BM26A**	**Date(s) of experiment:** **23 Oct -27 Oct 2014**	**Date of report:** **13 Feb 2015**
Shifts: 12	**Local contact(s): Dipanjan Banerjee**	

1. **Who took part in the experiments?** (Please indicate names and affiliations)
   Thilo Behrends (Utrecht University), Alwina Hoving (UU), Alejandra Morera (UU)
2. **Were you able to execute the planned experiments?**
   YES
   The experiment was very successful. We have been able to perform all the measurements we wished to perform.
3. **Did you encounter experimental problems?**
   NO, we had no significant problems.
   However, we had some problems with the fluorescence detector. The detector requires cooling with liquid N_2 . Filling the reactor with liquid N_2 is now automated and occurs once per day. However, a few hours before the refill, one of the elements of the detector elements produced a signal which was perturbed by electronic noise. After each N_2 refill, this deviating behaviour of one of the detector elements disappeared. It was no problem to exclude this element when calculating the X-ray absorption of the sample, so that the misbehaving element did not impair the quality of the XAFS spectra. However, as other elements of the detector are not operating any more, the replacement of the detector should be considered.

   From a spectroscopic point of view, we were surprised to see indications for photoinduced reduction of selenate which is adsorbed to clayey sediments. This is unexpected because the sample was installed in the cryostat and the low temperature should help to prevent beam-induced changes in the sample.

   When applying for beamtime, we did not know that the Chemistry Laboratory of the ESRF would not be available during the experiment due to renovation. However, we were informed about the situation in a timely manner so that we were able to adapt the planning accordingly: Instead of performing the experiments on the reaction of different Se species with Boom Clay material at the ESRF, we had performed these experiments before we went to the ESRF. These experiments were executed in a way that the samples for XAFS analysis were retrieved as shortly as possible before we had to leave to the ESRF. The wet pastes from the experiments were directly installed in sample holders which fit into the DUBBLE cryostat (thanks to Dr. Banerjee who provided us pictures and drawings of the holder so that we were able to built suitable sample holder), fixed with Kapton tape, sealed airtight directly after collection, frozen in liquid N_2, and kept frozen during transport and until measurement (< -70 C). By this, is was possible to reduce sample manipulation at the DUBBLE beamline to a minimum (removing the sample from the sealed bag, mounting them on the cryostat holder and installing them in the cryostat took only a few minutes and did not cause melting of the water in the sample. We assume that with this procedure, artefacts due to exposure to atmospheric oxygen could be avoided.
   Was the local support adequate?
   YES. The support was excellent. The beamline was perfectly prepared for the experiment so that we were able to collect the first spectra from our sample before lunchtime on the 23rd Oct. Dr. Banerjee has participated in several studies involving XAFS analysis of Se in natural samples. His expertise was a great help in the preparation and during the performance of the experiment.
   Are the obtained results at this stage in line with the expected results as mentioned on the project proposal?
   YES and NO. Many of the results agreed with expectations. In particular, XANES and EXAFS spectra

indicate that selenite was reduced to elemental selenium when being exposed to Boom Clay material. This finding is also in agreement with previous studies on interactions of selenite with Boom Clay. In contrast to previous studies, we retrieved material after different reaction periods (see Fig.1 as an example). This time series of spectroscopic information in combination with conventional analyses, which were performed during the experiments, enables us to quantify the contribution of adsorption and chemical reduction to the removal of dissolved selenite over time.

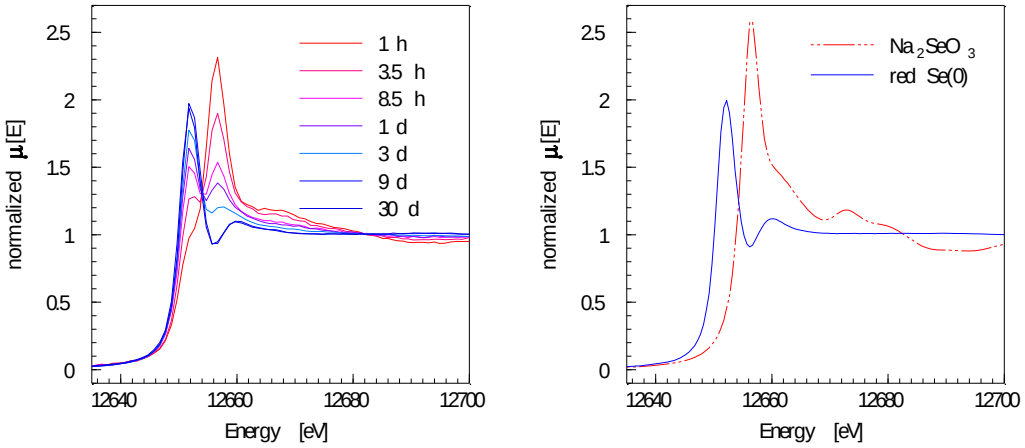

Fig 1. Left panel: Normalized XANES spectra of samples retrieved from experiments in which selenite was added to sterilized Boom Clay. In this experiment, the complete Boom Clay material was used without previous particle size separation. Comparison with spectra from reference materials (right panel) reveals that initially most of the selenium, which is associated with the solids, is in the form of selenite. Over time, the fraction of Se(0) increases, and after about 9 days reaction time all solid-bound selenium is Se(0).

Furthermore, we obtained time series from different Boom Clay size fractions. With these data it is possible to evaluate the dependency of selenite reduction kinetics on the particle size, and, in turn, relate them to the mineral assemblage which varies between the particle size fractions. A very interesting and not anticipated finding is that the clay fraction is more efficient than other size fractions to remove selenite from solution due to adsorption, but the strong adsorption seems to delay or inhibit chemical reduction. This result could be of importance for the safety assessment of nuclear waste repositories which are hosted in clay rich sediments.

The macroscopic results from the first series of experiments suggested that also selenate could be reduced by Boom Clay and by this become effectively immobilized. This observation was very unexpected. XAFS spectra show, indeed, that selenium occurred predominately in its elemental form in the samples. However, it was not possible to reproduce these results in the second experimental series and selenate showed only very low affinity for the solid phase and no indications for chemical reductions were obtained. The reason for this inconsistency in the results is enigmatic but we cannot definitely exclude the possibility that in the first experimental series accidently selenite instead of selenate was added.

4. Are you planning follow-up experiments at DUBBLE for this project?

YES. This experiment is part of the PhD project of A. Hoving and the possibility to perform follow-up experiments is highly desired and of pivotal importance for her project. An important goal of her project is to assess the effect of oxidation and reduction of Boom Clay on its interactions with selenium. In order to achieve this goal, similar experiments with redox manipulated Boom Clay are planned. From this experiment we have leaned that XAFS measurements are crucial for the correct interpretation of results from macroscopic experiments with Boom Clay and selenium.

5. Are you planning experiments at other synchrotrons in the near future?

YES, but not related to this or a comparable project.

6. Do you expect any scientific output from this experimental session (publication, patent, ...)

YES. The spectroscopic results obtained in this experiments complement the results from the diverse macroscopic experiments and create a coherent data set with several intriguing and innovative findings. The goal is to submit a manuscript until summer 2015.

7. Additional remarks

We are very grateful that NWO supports this excellent facility. The opportunity to perform standard bulk XAFS measurements is of great value for our research and the DUBBLE beamline is perfectly suited for our needs.