ESRF	**Experiment title:** Se K-edge XAS of the valence and lo cal environment of selenium in glas ses to enable increased retention f or environmental benefit	**Experiment number**: HD-372
Beamline: BM08	**Date of experiment**: from: 22 April 2009 to: 26 April 2009	**Date of report**: February 2010
Shifts: 12	**Local contact(s)**: Francesco d'Acapito	*Received at ESRF:*

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Report:

This study formed part of our ongoing research into the behaviour and structural environment of selenium in oxide glasses. Selenium is an element about which relatively little is known in oxide glasses yet it enjoys widespread use in a range of industrial and environmental applications.

Se K–edge XANES and EXAFS were collected on BM08 for a suite of crystallographically well-characterised standard materials and also for 10 oxide glasses containing an estimated 50–1000 ppm of Se. Analyses were conducted simultaneously in fluorescence and transmission modes with the samples present as pressed discs consisting of intimate mixtures of powdered (<75um) sample and cellulose acetate. Sample thicknesses were calculated to provide optimum absorption cross sections for transmission samples (i.e. the standards). Sample discs, once prepared, were placed in the beam line sample holder and subjected to vacuum prior to measurement.

Standard materials included Na_2SeO_4 (Se^{6+}); SeO_2, Na_2SeO_3 and $BaSeO_3$ (Se^{4+}); Se (Se^0); CdSe, ZnSe and BaSe (Se^{2-}) and the suite of oxide glasses provided measurable Se contents for XANES and EXAFS. We acquired Se K–edge XANES and EXAFS between 12,440 eV and 13,500 eV. The EXAFS energy range provided a *k*–range of 0–14 Å. A number of data sets were acquired for each sample to improve the signal – to – noise ratio.

The beam time was highly successful and high quality data was acquired, despite the loss of some beam time due to problems with the beam.

Fitting of sample XANES and EXAFS is currently underway using the Athena and Artemis software packages. Following data reduction, the Se K−edge EXAFS data will be analyzed

using appropriate software to extract average first shell and potential second shell distances and coordination

Preliminary results show that the behaviour of the K-edge energies of Se standards as a function of formal Se valence broadly mimic the behaviour of sulphur, which we have recently studied, and which exhibits an approximately linear decrease in K-edge energy with decreasing formal Se valence. Differences in the ionic/covalent nature of the metal – Se bond in selenide standards leads to differences in the K-edge energy; however, this behaviour is broadly consistent with that observed previously for sulphur standards. Unfortunately the K-edge energies of Se^0 and some Se^{2-} compounds overlap, making elucidation of Se valence difficult (based on edge energy) for sample glasses.

Preliminary XANES results for the glass samples demonstrate that the dominant Se valence changes, as expected, a function of glass preparation conditions (pO_2). However, given the difficulty in discerning the difference between Se^0 and lower Se oxidation states, it can only be stated that in the most strongly reduced glasses there is spectroscopic evidence for the presence of Se^0 or lower Se valences.

Preliminary EXAFS results are currently providing Se-ligand distances consistent with the oxidation state/s present in each sample, however, data processing is still underway and more definitive conclusions cannot yet be given.

A manuscript is currently in preparation to discuss the data resulting from this beam time allocation. It is fully anticipated that the manuscript will be submitted to a primary journal for publication during 2010.