



	Experiment title: Chlorine XAS and XES in Glasses for Radioactive Waste Immobilisation: a Study of its Structural Role	Experiment number: EC-739
Beamline: ID26	Date of experiment: from: 10 February 2011 to: 15 February 2011	Date of report: August 2016
Shifts: 15	Local contact(s): Pieter Glatzel	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Paul A. Bingham, University of Sheffield, UK (now at Sheffield Hallam University, UK)		

Report:

This study formed part of our ongoing research into the behaviour and structural environment of chlorine in oxide glasses. It also contained aspects of another beam time proposal, HD-503 XANES and XES of Sulphur in Oxide Glasses for Waste Immobilisation.

Cl K-edge XANES and EXAFS and S K-edge XAS and XES were collected on ID-26 for a suite of crystallographically well-characterised standard materials and also for several oxide glasses doped with different levels of Cl and S, and prepared under different oxidation conditions.

Samples were powdered to 75 microns and mounted onto an Al plate using acetone. The incident energy was controlled on the beamline utilising a fixed-exit double Si (111) crystal monochromator. Collimating and harmonic rejection mirrors were used to remove higher order harmonics. The theoretical resolution of the XAS experiment was 0.36 eV at the S K-edge. The energy was calibrated by using the absorption edge of natural S at 2472.0 eV. For XAS experiments the data were collected utilising a fluorescence detector mounted at 45° from the incident X-ray beam. The incident X-ray energy was varied over a range of 2450–2550 eV. XES experiments were carried out utilising a Johansson type crystal spectrometer employing a Si (111) crystal which was curved cylindrically to meet a 500 mm Rowland circle radius, and a thermoelectrically cooled CCD detector (pixel size 22.5 x 22.5 micron). The incident photon energy was tuned to 2.52 keV. The sample surface was mounted at 45° and the X-ray fluorescence was collected at 90° with respect to the incident beam direction. The energy calibration was performed relative to the Ka line of native S (2307.89 eV) which was used as a reference. The overall experimental energy resolution was 0.4 eV, which was high enough to separate clearly between the S₂₋ and S₆₊ emission lines and quantitatively determine the proportion of reduced sulphur species in the sample. The latter was performed

by fitting the measured XES spectra with a combination of two individual Lorentzian line shape doublets, corresponding to the emission lines associated with S2- and S6+, respectively

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 and also due to issues with the beamline.

Data were successfully processed and have resulted in the following publications:

O.J. McGann, P.A. Bingham, R.J. Hand, A.S. Gandy, M. Kavčič, M. Žitnik, K. Bučar, R. Edge, N.C. Hyatt, The effects of gamma-radiation on model vitreous wastefoms intended for the disposal of intermediate and high level radioactive wastes in the United Kingdom, *Journal of Nuclear Materials* 429 (2012) 353-367.

O. J. McGann, PhD Thesis, University of Sheffield, UK, 2013.