



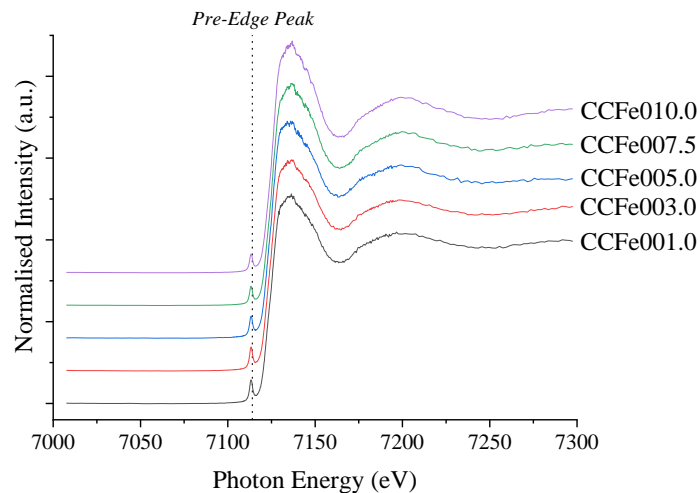
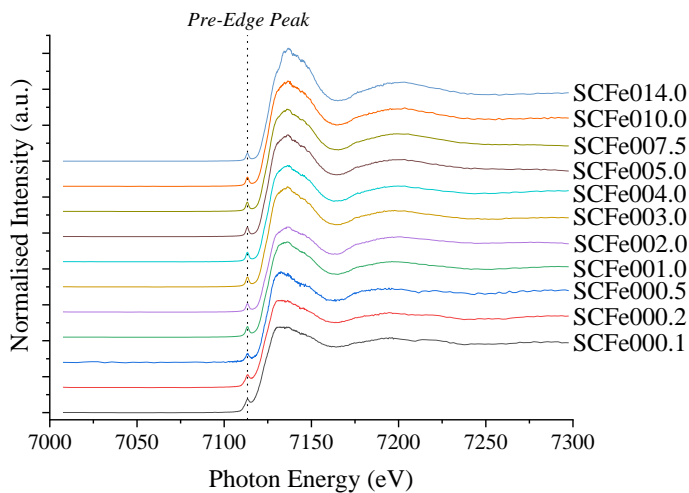
	Experiment title: Investigation of Fe, Cr, Mn, Ni and Ce oxidation states to support vitrification of simulated high-iron radioactive wastes	Experiment number: MA-4906
Beamline:	Date of experiment: from: 05/02/2021 to: 09/02/2021	Date of report:
Shifts:	Local contact(s): Paul Thompson	<i>Received at ESRF:</i>
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Report:

The primary goals of this proposal was to studying the effect on foaming behaviour by the multivalent transition metal species, in support of a large scale nuclear waste vitrification project underway at the Hanford site, USA. As well as the primary prosed body work, a secondary body of work took place during this experimental period, which focused on the chemistry of varying concentrations of iron within borosilicate glasses. Two series of glass were investigated as part of this work; a simple sodium borosilicate glass, and a more complex borosilicate glass, with the increased complexity coming from additional glass forming oxides. Some of the wastes expected at the Hanford site are expected to have high concentrations of iron oxide, so furthering the undertanding of the iron chemistry in borosilicate glass is necessary.

Iron K-edge XANES was carried out on both series of borosilicate glasses, to determine the valency of the iron in each sample, and if the valency changes with changing iron oxide concentrations. Each sample was measured at the BM28 beamline, with an energy range of with an energy step of xxx between xxx to acquire as much detail of the pre-edge and edge features as possible. Standard Fe-bearing minerals were measured alongside the samples. The minerals contained Fe(II), Fe(III), and mixed valency iron. These standards were used to correct for any energy drift unique to the beam on the day of measurement by comparing energy values of key spectral features (the 1s – 3s transition pre-edge peak was used) with values from published literature, and determining a constant energy offset. It was determined there was an offset of -2.42 eV. This offset was then applied to the energy of all samples.

The sample spectra were normalised in ATHENA, with repeated measurements averaged to provide the best S/N spectra for each sample. The stackplot of the processed spectra can be seen in *Figures 1a & 1b*.



Figures 1a & 1b: Fe K-edge Stackplots for both series investigated.

For each sample investigated, the 1s – 3s pre-edge peak (marked on **Figures 1a & 1b**) is used to determine the valency of the iron. This was done by determining the centroid position of the pre-edge peak, and comparing this centroid position with measured standard minerals, and

previous research. **Figure 2** shows that the samples all have a similar pre-edge centroid values that are close to the indicated Fe(III) position on the graph. However, there is an element of ambiguity, as the centroid values appear to be comparable to magnetite, which has both Fe(II) and Fe(III). To aid with this, Fe⁵⁷ Mössbauer spectra was acquired for the high-Fe samples alongside the XANES data to guide the interpretation of data. The Mössbauer spectra showed that all measured samples had spectral features that corresponded to Fe(III) but none that suggested the presence of any Fe(II). When compared with the data in **Figure 2**, this would suggest that the iron within the high-Fe samples exists as Fe(III). This can be extended to the low-Fe samples, as the centroid positions for the low-Fe samples are comparable to the high-Fe samples.

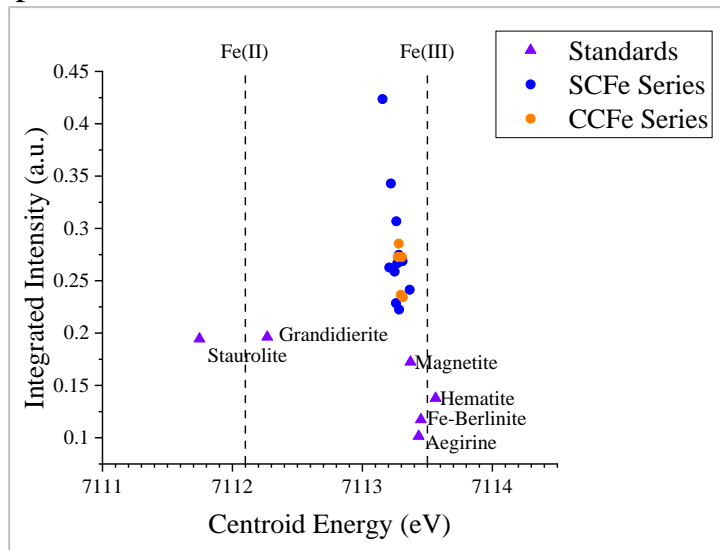


Figure 2: The average centroid positions for all measured samples and standards.

In conclusion, Fe K-edge XANES was used to help determine the valency of the iron across two different borosilicate glass series by using the 1s – 3s pre-edge peak. While there was some ambiguity due to the position of the centroid suggesting there may be some Fe(II), the data provided by the XANES spectra in combination with Mössbauer spectra on the high-Fe samples, showed that the iron exists as Fe(III) within the samples. Further work would be to look at determining the average coordination number of the iron within these glasses, to determine whether there is 4, 5, or 6 coordinated iron within the glass. Each coordination has a unique role within a glass network.