Characterisation of sodium iron phosphate glass loaded with simulant nuclear fuel

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1 Introduction

The UK holds a significant quantity of degraded nuclear fuel from research and decommissioning activities. Approximately 200 teHM of this inventory is clad with or stored using stainless-steel materials, in many cases degradation would prevent de-cladding prior to processing of the actinide components [1], [2]. A relatively novel method for immobilization of such materials, details the total chemical dissolution of degraded fuel using a similar chemistry to that of the PUREX process [3], followed by a pre-calcination step and vitrification with a sodium-iron phosphate glass composition.

The relation of iron oxidation state to chemical durability in aqueous environments has been well established in literature [4]. Optimal redox behaviour describes speciation of Fe^{3+} ions to facilitate substitution of poor durability P-O-P bonding structures with the higher durability P-O-Fe counterparts.

2 Experiment

Sodium iron phosphate glass was batched with a base composition of ~61/18/9/7/5 mol.% of P_2O_5/Fe_2O_3/Na_2O/ SiO_2/Al_2O_3, using reagent grade oxides as precursors and $(NH_4)H_2PO_4$ as a phosphate source. This base glass will be further represented as IPSAS (iron phosphate sodium iron silicate). 0-14 mol.% CeO_2 was added to each base composition as the fuel simulant, followed by homogenisation, 6 hrs pre-calcination at 600 °C, followed by melting at a range of temperatures between 1250 - 1450 °C, casting and annealing at 550°C for 4 hrs – all under an air atmosphere.

Pulverised samples of annealed glass were diluted with PEG with addition masses selected for the relative cross-section at the Fe-K edge. XANES spectra were collected in transmission mode at BL-27B. Standards of Fe_3O_4, $Fe_3(P_2O_7)_2$, $Fe_3(PO_4)_2$ were also prepared and measured. The Athena software package was used to correct and align data, before use of a gaussian fitting function to integrate the area under the pre-edge features ad determine the centroid position.

3 Results and Discussion

Figure 1 shows the result from integration of the pre-edge features for the IPSAS glass compositions with 0 mol.% CeO_2 melted at two different temperatures. A significant variation in the higher 1450 °C melt sample is the larger contribution at a slightly lower energy, shifting the centroid position, indicating a change in iron oxidation state. Figure 2 details the centroid positions for IPSAS samples melted between 0 – 15mol.% CeO_2 at

temperatures of 1250 – 1450 °C, with reference compounds used to delineate Fe^{2+} and Fe^{3+} speciation. A clear correlation shows a decrease of average oxidation state with increasing melt temperature.
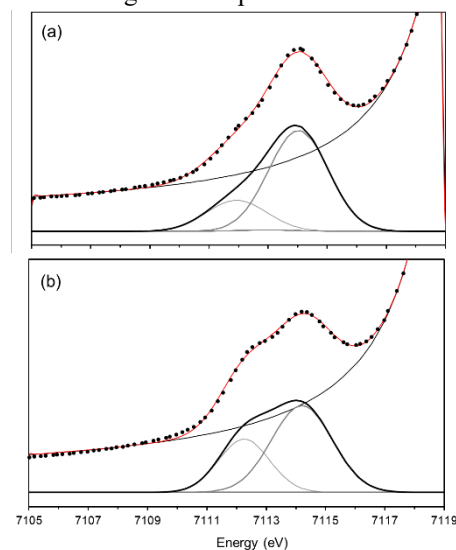

Fig. 1: Pre-edge features of the Fe-K edge data for IPSAS melted at 1350 °C (a) and 1450 °C (b).
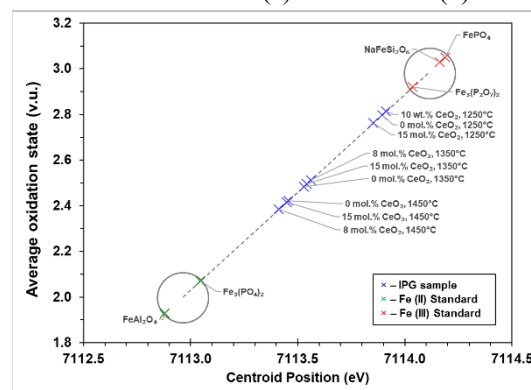

Fig. 2: Average oxidation state of IPSAS glass samples plotted with Fe (II) and Fe (III) reference standards

References
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