Comment on “Preliminary assessment of modified borosilicate glasses for chromium and ruthenium immobilization”, by Farid and Rahman.

Neil C. Hyatt,* Claire L. Corkhill, Daniel J. Bailey, Adam J. Fisher, and Russell J. Hand

Immobilisation Science Laboratory, Department of Materials Science and Engineering, The University of Sheffield, S1 3JD, UK

* Corresponding Author; email: n.c.hyatt@sheffield.ac.uk

Abstract

Farid and Rahman recently reported an investigation of the microstructure and alteration of borosilicate glasses designed for the immobilisation of UK radioactive wastes [*Preliminary assessment of modified borosilicate glasses for chromium and ruthenium immobilization*, Materials Chemistry and Physics, 186 (2017) 462-469]. The authors draw conclusions concerning the partitioning of elements within two devitrified spinel phases, at variance with previous studies of these materials. The authors also present solution chemistry and surface analysis data for alteration of these glasses, and postulate micro-cracks apparent in the gel layer of the altered glass to govern the extent of alteration. From analysis of data presented by Farid and Rahman, and comparison with previous studies, we show that their data are consistent with the presence of a single spinel phase of complex chemical composition, $(\text{Mg,Zn,Ni})(\text{Cr,Fe,Al})_2\text{O}_4$. We show the chemistry and surface analysis data presented by Farid and Rahman to be contradictory, in terms of the relative alteration behaviour of these glasses, as verified by previous studies, and deduce that an alternative explanation is required to rationalise their observations. We also comment on other aspects of the report which require clarification.

Keywords: radioactive waste, glass matrix, structure immobilisation.

1. Introduction

In a recent publication, Farid and Rahman reported an investigation of alkali borosilicate glasses applied for the immobilisation of UK radioactive wastes [1]. Aspects of this study are inconsistent with previous investigation of these materials [2-5] and require clarification, as we highlight in this comment on their study.

In the UK, and internationally, alkali borosilicate glasses are the material of choice for vitrification of the fission products and minor actinides arising from nuclear fuel reprocessing, classified as High Level Waste (HLW) [2-7]. Modification of the UK HLW glass composition, by addition of CaO and ZnO, has been studied with the aim of improving processing characteristics and long term durability, as discussed elsewhere [2-6].

2. Analysis of glass microstructure

To fully understand the dependence of HLW glass properties on ZnO content, it is necessary to appreciate the role of Zn in the glass structure, i.e. whether a network modifier, network intermediate, or network former. In their contribution, Farid and Rahman erroneously state Zn to be a network modifier in such glasses [1], which they infer to influence the incorporation of Cr within the glass and accessory spinel phase(s). In fact, Zn K-edge X-ray absorption spectroscopy has demonstrated Zn to primarily participate in network formation in such glasses, as ZnO_4 polyhedra (Zn-O distance of $1.95 \pm 0.01 \text{ \AA}$), linking, on average, to $2 \pm 1 \text{ SiO}_4$ units *via* bridging oxygen atoms [2]. This conclusion was later verified by Raman spectroscopy investigation and molecular dynamics simulations of the structure of closely related UK HLW glass compositions [3, 4].

Farid and Rahman focus on the presence of crystalline RuO_2 and Cr_2O_3 bearing phases within a CaO and ZnO modified glass, prepared in our laboratory, for the immobilisation of HLW derived principally from Magnox fuel reprocessing [2, 4, 5]. Farid and Rahman incorrectly attribute the source of Cr_2O_3 in this glass to *“the result of Magnox cladding and dissolution processes”* [1]. However, the composition of Magnox fuel cladding is devoid of Cr, being an alloy of Mg with 0.8% Al and 0.002-0.05 % Be, by weight [8]. In fact, the source of Cr is principally the corrosion of stainless steel process equipment and storage vessels [7], by the acidic HLW raffinate. In the case of “blended” glass compositions derived from HLW arising from reprocessing of Magnox and Advanced Gas-cooled Reactor (AGR) fuels, a contribution from leaching of AGR cladding during fuel dissolution is also likely (AGR cladding composition approximately: Fe 52.72%, Cr 20.4%, Ni 25.1%, Nb 0.60, other 1.18%, by weight [9]).

Farid and Rahman report the presence of two distinct spinel phases in their Magnox glass material, formulated ZnCr_2O_4 and $\text{Fe}_{0.23}\text{Mg}_{0.70}\text{Al}_{1.97}\text{O}_4$. However, we suggest that this conclusion is not adequately supported by the X-ray diffraction or SEM / EDX data presented by the authors.

Regarding the X-ray diffraction data (Figure 1 in [1]), the Bragg reflections may be indexed uniquely as a mixture of RuO_2 and a single spinel phase AB_2O_4 (space group $\text{Fd}\bar{3}\text{m}$), as shown by inspection of Table 1 and Figure 1 presented here (note, reference diffraction patterns in Figure 1 were extracted from the ICSD database [10]). The presence of a second cubic spinel phase would require double the number of observed spinel reflections; however, such additional reflections are not present at appreciable intensity, as assessed against the signal to noise ratio of the published data (compare Figure 1 here with Figure 1 in [1]). Farid and Rahman did not report the optical arrangement and detector configuration for their X-ray diffractometer, but a typical maximum step size is 0.02° for a laboratory instrument. This should be sufficient to resolve the distinct Bragg reflections of ZnCr_2O_4 and $\text{Fe}_{0.23}\text{Mg}_{0.70}\text{Al}_{1.97}\text{O}_4$, if both phases were present in appreciable concentration, as shown by the reference diffraction patterns in Figure 1.

Regarding the SEM / EDX data, the *area* EDX spectrum labelled (iv) of Figure 3 in [1], shows the presence of Mg, Al, Cr, Fe, Ni and Zn in high concentration, associated with observable crystallites, compared to EDX spectrum labelled (iii), associated with the Magnox glass matrix. Mg, Cr, Fe, Ni and Zn are known spinel constituents and, together with the available X-ray diffraction data, it is reasonable to infer that the observed crystallites are indeed a complex spinel. However, because the EDX data are acquired from a wide *area*, and not from *points* within the crystallites, it cannot be concluded that there are two spinel phases present of distinct composition. Indeed our studies of very closely related glass compositions identified only a single spinel phase of composition $(\text{Zn}_{0.60}\text{Ni}_{0.20}\text{Mg}_{0.20})(\text{Cr}_{1.37}\text{Fe}_{0.63})\text{O}_4$ [4], which is broadly consistent with both the EDX data (Figure 3 (iv)) and X-ray diffraction data (Figure 1) presented by Farid and Rahman [1]. Note that although the glasses reported in our study did not contain RuO_2 , this is not expected to significantly affect the chemical composition of the spinel given the very low solubility of RuO_2 in the glass phase [11].

A key conclusion of the study by Farid and Rahman is that *“Published results showed that spinel, containing chromium, iron, and nickel, is the main crystalline phase that immobilizes chromium. These results are not confirmed in this study, where the presence of zinc oxide (as modifier) has affected the nature of chromium immobilization.”* [1]. We infer from this statement that the authors assert the incorporation of Cr into a spinel phase of composition ZnCr_2O_4 . As noted above, within the borosilicate glass phase, Zn acts as a network former, not a modifier.

Comparison of the reference diffraction patterns of ZnCr_2O_4 and $\text{Fe}_{0.23}\text{Mg}_{0.7}\text{Al}_{1.97}\text{O}_4$, Figure 1, showed that the ZnCr_2O_4 to be a better fit to the spinel phase in the X-ray diffraction data of Farid and Rahman (based on positions of the Bragg reflections). However, this cannot be relied on as a conclusive identification of a phase of this specific composition, as appears to be the assumption of Farid and Rahman, since the cubic spinel structure is highly flexible toward isomorphic substitution. Indeed, as discussed above, the SEM/EDX data presented by Farid and Rahman are consistent with incorporation of Zn and Cr within a chemically complex spinel, similar to $(\text{Zn}_{0.60}\text{Ni}_{0.20}\text{Mg}_{0.20})(\text{Cr}_{1.37}\text{Fe}_{0.63})\text{O}_4$ reported previously [4].

3. Surface analysis of pristine and altered glasses

Farid and Rahman also present results of SEM observations of pristine and altered glass surfaces. Figure 2 in [1] shows the surface of a pristine glass specimen with the composition Na_2O 11.1%, Li_2O 5.3%, B_2O_3 21.9%, SiO_2 61.7% (by weight), which is commonly referred to as MW glass – this is the glass frit composition used to vitrify calcined HLW at the Sellafield site [4-7]. The features labelled (i) and (ii) in Figure 2 of [1] are interpreted as “*inclusions*” due to the presence of “*bubble and/or immiscible components*”. Farid and Rahman note that the EDX spectra for these features “*are similar and detect only structural elements (Si, Na, O)*” of the glass matrix [1]. Figure 2 is evidently a secondary electron image, given the topography apparent in features (i) and (ii), which are clearly situated on top of the polished glass surface, inconsistent with the interpretation as “*inclusions*” due to the presence of “*bubble and/or immiscible components*”. The fact that the EDX spectra of these features are essentially indistinguishable from the glass matrix suggests that the features are either: a) glass particulates of the same composition as the matrix, or b) a material of low atomic number, permitting transmission of the electron beam and the characteristic X-rays emitted from the glass sub-surface. The rounded edges of the features in question are inconsistent with glass particulates produced by brittle fracture in specimen preparation or handling, which are typically characterised by sharp edges. Taken together, these observations are consistent with features (i) and (ii) being associated with extraneous organic matter on the surface of the glass sample, rather than “*bubble and/or immiscible components*”. We note that the EDX spectrum associated with feature (i), Figure 2(b) in [1], exhibits a weak C K α emission line, which could be consistent with the presence of organic material, although we cannot rule out a contribution from the carbon coating applied by the authors.

In the examination of altered glass samples, Farid and Rahman report “*Samples morphologies are altered by the presence of pitting associated with micro-cracks of different sizes e.g. 3–5 μm and white fibers (Fig. 5 a&b). BE-SEM of simulated Magnox-modified glass shows micro-cracks*

network that surrounds and connects between the pittings (Fig. 5c)"; where the figure numbers refer to [1]. Aqueous corrosion of glasses involves a complex series of reactions, including hydration, ion exchange, network hydrolysis, and network condensation, resulting in an interfacial alteration layer, the "gel layer", which is depleted in soluble elements. The micro-cracks observed by Farid and Rahman are, in fact, typical of desiccation of the glass gel layer, leading to a decrease in the molar volume and development of tensile stress with respect to the underlying pristine material. Ultimately, cracks open in the gel layer to relieve this tensile stress, as highlighted by Icenhower and Steefel [12].

Finally, we highlight an apparent inconsistency in the SIMS and solution chemistry data associated with dissolution of the reference (MW) and compositionally modified simulant Magnox glass, presented by Farid and Rahman [1]. The reported normalised mass loss of boron from the reference (MW) glass ($0.13 \text{ g m}^{-2} \text{ d}^{-1}$) is three times greater than for the compositionally modified Magnox glass ($0.05 \text{ g m}^{-2} \text{ d}^{-1}$), Table 2 in [1]. The elemental SIMS profiles are consistent with these data, with apparent depletion of B, Li, Na and Si to a depth of >400 nm for the reference (MW) glass and 270nm for the compositionally modified simulant Magnox glass (compare Figure 4a / 7a, and Figure 4b / 7b, respectively, in [1]). Evidently, alteration of the reference (MW) glass occurred to a greater depth than the compositionally modified simulant Magnox glass. This is as expected, due to the incorporation of less soluble metal oxide constituents present in the HLW stream, and the lower proportion of soluble glass constituents (Na_2O , Li_2O , and B_2O_3), in the simulant Magnox composition (Table 1 in [1], see also [4, 5]). Our recent vapour phase hydration study of such glasses validate these findings, with the alteration rate of MW glass ($24.8 \pm 2.5 \text{ g m}^{-2} \text{ d}^{-1}$) much greater than for the compositionally modified Magnox glass ($0.9 \pm 0.3 \text{ g m}^{-2} \text{ d}^{-1}$) [5]. Note that although the experimental conditions of the two studies are very different, the relative glass durability is expected to be differentiated. In this context, the SIMS determined H^+ depth profiles of the altered surfaces of these glasses, reported by Farid and Rahman, Figure 8 in [1], are difficult to comprehend. Since the solution chemistry data and elemental SIMS profiles of the reference (MW) composition show this to be more extensively altered than the compositionally modified Magnox glass, it could be expected that the H^+ concentration should be greater in the altered surface of the former, compared to the latter. However, Figure 8 in [1] shows the opposite to be true. Farid and Rahman state that with respect to the compositionally modified Magnox glass, *"This could be attributed to the presence of micro-cracks network on the surface, these cracks acts as pathway for water molecules"*. This does not seem a plausible explanation, given the uncertainty over the origin of the cracks in the glass gel layer discussed above, which are consistent with post-alteration desiccation of the gel layer. Moreover, such cracks were also observed on the surface of the

altered reference (MW) glass, as shown in Figure 6(a) of [1]. A possible explanation for the discrepancy in reported H⁺ SIMS profiles might be different storage conditions, and hence desiccation, of the glass gel layers, potentially assisted by different permeability. Alternatively, Figure 6(a) of [1] shows areas of the altered surface of the reference (MW) glass where the gel layer has spalled, revealing the underlying substrate. The inconsistency in the SIMS H⁺ profiles of Figure 8 of [1] could be rationalised if the data associated with the altered reference (MW) glass were to correspond with the underlying substrate on an area of the surface from which the gel layer had spalled. Further investigation of this apparent discrepancy is warranted.

4. Conclusions

The microstructure of the compositionally modified Magnox glass reported by Farid and Rahman [1], is consistent with that previously reported for closely related materials, with Cr incorporated within a single (Mg,Zn,Ni)(Cr,Fe,Al)₂O₄ spinel phase [4]. The relative alteration of the reference MW and compositionally modified Magnox glass reported by Farid and Rahman [1], as determined by analysis of solution chemistry, is consistent with both aqueous and vapour phase alteration studies of closely related materials [4, 5]. However, the corresponding H⁺ SIMS profiles reported by Farid and Rahman appear contradictory with their solution chemistry data and that previously published [4, 5]. The reconciliation of this contradiction advocated by Farid and Rahman, involving water penetration through micro-cracks evident in the gel layer, seems specious, given the resemblance of the micro-cracks, present on both glasses, to those arising from post-alteration desiccation of the hydrated gel layer [12].

Overall, this study highlights the need for careful interpretation of glass microstructure and corrosion behaviour, to provide the robust data and mechanistic understanding required to support a safety case for radioactive waste disposal, which will engender scientific and public confidence. To address this key knowledge gap, recent studies have reported new data and mechanistic understanding of the dissolution behaviour of UK HLW glasses [13, 14].

Acknowledgements

We acknowledge financial support for our research reported here from EPSRC under grants EP/L014041/1, EP/L015390/1, EP/G037140/1, and EP/N017374/1. Fisher is grateful to RWM Ltd., for studentship support. This research was performed, in part, at the MIDAS facility, at the University of Sheffield, which was established with support from the Department of Energy and Climate Change. Although some of the authors provided materials for the study of Farid and Rahman [1], this should not be taken as an endorsement of the methods or conclusions of their investigation.

References

1. O.M. Farid and R.O.A. Rahman, Preliminary assessment of modified borosilicate glasses for chromium and ruthenium immobilization, *Materials Chemistry and Physics*, 186 (2017) 462-469.
2. N.J. Cassingham, M.C. Stennett, P.A. Bingham, N.C. Hyatt, and G. Aquilanti, *The Structural Role of Zn in Nuclear Waste Glasses*, *International Journal of Applied Glass Science*, 2 (2011) 343-353.
3. T.R. Stechert, M.J.D. Rushton, and R.W. Grimes, *Predicted Mechanism for Enhanced Durability of Zinc Containing Silicate Glasses*, *Journal of the American Ceramic Society*, 96 (2013) 1450-1455.
4. H. Zhang, C.L. Corkhill, P.G. Heath, R.J. Hand, M.C. Stennett, and N.C. Hyatt, *Effect of Zn- and Ca-oxides on the structure and chemical durability of simulant alkali borosilicate glasses for immobilisation of UK high level wastes*, *Journal of Nuclear Materials*, 462 (2015) 321-328.
5. N.J. Cassingham, C.L. Corkhill, M.C. Stennett, R.J. Hand, and N.C. Hyatt, *Alteration layer formation of Ca- and Zn-oxide bearing alkali borosilicate glasses for immobilisation of UK high level waste: A vapour hydration study*, *Journal of Nuclear Materials*, 479(2016) 639-646.
6. R. Short, *Phase separation and crystallisation in UK HLW vitrified products*, *Procedia Materials Science*, 7 (2014) 93-100.
7. M.T. Harrison, *The effect of composition on short- and long-term durability of UK HLW glass*, *Procedia Materials Science*, 7 (2014) 186-192.
8. G. Marsh and H. Eccles, *Fuel fabrication*, in: *The Nuclear Fuel Cycle: From Ore to Waste*, ed. P.D. Wilson, Oxford University Press (1996) pp40-66
9. R. C. Ecob, R. C. Lobb, and V.L. Kohler, *The formation of G-phase in 20/25 Nb stainless steel AGR fuel cladding alloy and its effect on creep properties*, *Journal of Materials Science*, 22 (1987) 2867-2880.
10. Inorganic Crystal Structure Database, FIZ Karlsruhe, available at: <http://icsd.fiz-karlsruhe.de>

11. W. Lutze, F.C. Perez-Cardenas, K.S. Matlack, I.L. Pegg and P. Schill, *"Testing and modelling the behaviour of platinoids during vitrification of high level radioactive waste. Part 1"*, Glass Technology.: European Journal of Glass Science & Technology A, 48 (2007) 263-275
12. J.P. Icenhower and C.I. Steefel, *Dissolution rate of borosilicate glass SON68: A method of quantification based upon interferometry and implications for experimental and natural weathering rates of glass*, Geochimica et Cosmochimica Acta, 157 (2015) 147–163.
13. N. Cassingham, C.L. Corkhill, D. Backhouse, R.J. Hand, J.V. Ryan, J.D. Vienna, and N.C. Hyatt, *The initial dissolution rates of simulated UK Magnox-ThORP blend nuclear waste glass as a function of pH, temperature and waste loading*, Mineralogical Magazine, 79 (2015) 1529-1542.
14. C.L. Corkhill, N. Cassingham, P.G. Heath, and N.C. Hyatt, *Dissolution of UK High-Level Waste Glass Under Simulated Hyperalkaline Conditions of a Colocated Geological Disposal Facility*, International Journal of Applied Glass Science, 4 (2013) 341-356

Table

Bragg reflection 2θ (°)	Phase	Assignment
28.1	RuO ₂	(110)
30.5	AB ₂ O ₄	(220)
35.8	AB ₂ O ₄	(311)
40.1	RuO ₂	(200)
43.4	AB ₂ O ₄	(400)
54.3	RuO ₂	(211)
57.5	AB ₂ O ₄	(511)
58.0	RuO ₂	(220)
59.9	RuO ₂	(002)

Table 1: Analysis of X-ray diffraction data presented in Figure 1(b) of [1], showing the presence of only one significant spinel phase.

Figure