

Discussion

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



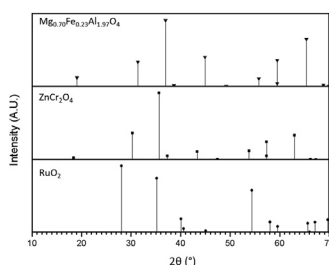
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HIGHLIGHTS

- Inaccuracies in the report of Farid and Rahman, on UK HLW glasses, are clarified.
- A single complex spinel phase incorporates Zn and Cr, consistent with earlier studies.
- SIMS data of Farid and Rahman are apparently inconsistent with solution chemistry data.

GRAPHICAL ABSTRACT



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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.

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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].

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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 ± 0.01 Å), linking, on average, to 2 ± 1 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 decladding 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 20.40%, Ni 25.10%, 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 (Fig. 1 in Ref. [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 Fig. 1 presented here (note, reference diffraction patterns in Fig. 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 Fig. 1 here with Fig. 1 in Ref. [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

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

Bragg reflection 2θ ($^\circ$)	Phase	Assignment
28.1	RuO_2	(110)
30.5	AB_2O_4	(220)
35.8	AB_2O_4	(311)
40.1	RuO_2	(200)
43.4	AB_2O_4	(400)
54.3	RuO_2	(211)
57.5	AB_2O_4	(511)
58.0	RuO_2	(220)
59.9	RuO_2	(002)

both phases were present in appreciable concentration, as shown by the reference diffraction patterns in Fig. 1.

Regarding the SEM/EDX data, the *area* EDX spectrum labelled (iv) of Fig. 3 in Ref. [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 (Fig. 3 (iv)) and X-ray diffraction data (Fig. 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 was 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 $\text{Fe}_{0.23}\text{Mg}_{0.70}\text{Al}_{1.97}\text{O}_4$, Fig. 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].

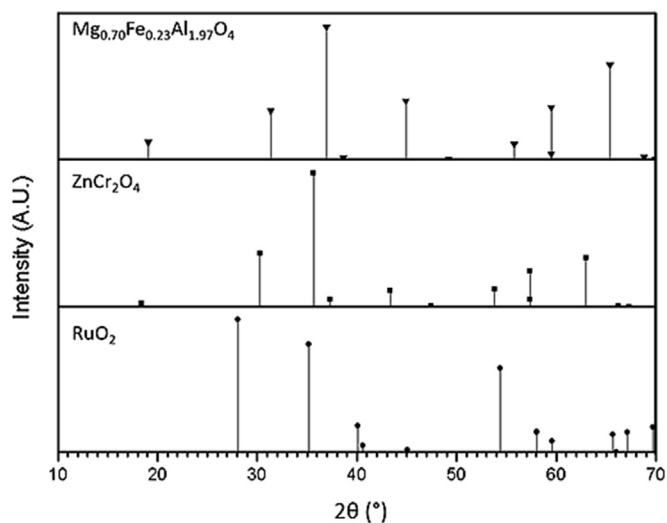


Fig. 1. Reference X-ray diffraction patterns for $\text{Mg}_{0.70}\text{Fe}_{0.23}\text{Al}_{1.97}\text{O}_4$, ZnCr_2O_4 , and RuO_2 , from the ICSD database (records: 89056, 290018, 172178 respectively [10]); data are for Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å.

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