An Investigation into the Oxidation State of Molybdenum in Simplified High Level Nuclear Waste Glass Compositions

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The redox state of Mo in glasses containing simplified simulated high level nuclear waste (HLW) streams has been investigated using Electron Spin Resonance (ESR) and X-ray Photoelectron Spectroscopy (XPS). Melts performed in highly oxidising or neutral (air) atmospheres contained Mo^{6+}, but our study indicates that the Mo can be at least partially reduced to Mo^{4+} or Mo^{3+} by melting in a reducing atmosphere. The implications for glasses containing a full simulated HLW stream are that the formation of detrimental crystalline phases containing Mo^{6+} upon heat treatment may be avoided by reducing the oxidation state of Mo during melting.

INTRODUCTION

Alkali borosilicate glasses are used by British Nuclear Fuels (BNFL) to vitrify HLW raffinates originating from the reprocessing of spent nuclear fuel. Experiments using simulated nuclear waste streams have shown that if the waste loading in these glasses is high (i.e.>20wt%), the glasses may undergo devitrification, which can have detrimental effects on the chemical durability [1]. When Mo is present in concentrations greater than 1wt% the potential for devitrification is increased. The crystalline phases that Mo forms with other fission products are generally termed yellow phase. Yellow phase consists of a mixture of alkali sulphates, chromates and molybdates. Some yellow phase can be highly water soluble and the vitrification process should be optimised in order to minimise its formation.

Experiments were performed using a full simulated HLW stream based upon 4:1 ratio of high burn up UO_2/mixed oxide (HBU/MOX) fuel reprocessed waste, a composition currently being considered for vitrification in the future. As part of a study into the devitrification of HLW glasses, compositions containing elevated waste loadings of up to 35wt% stimulant waste have been prepared, and it was found that at these waste loadings, these glasses tended to devitrify upon heat treatment (representing the slow cools of the real vitrification product) and the crystalline phase formed was a powellite type molybdate analogous to yellow phase [2]. The Mo in these molybdate phases was hexavalent in the form of $(MoO_4)^{2-}$ ions. It was suspected that if the oxidation state of the Mo could be lowered during the melting process, the formation of powellite type molybdates upon heat treatment could be avoided. This paper is a review of ongoing experiments designed to investigate the oxidation state of Mo in glasses containing a simplified version of the simulated HLW stream (in order to simplify analysis of results). Whilst Mo redox in silicate glasses has been investigated before [3,4] the aims of this paper were to investigate Mo redox behaviour under varying redox conditions in an alkali borosilicate glass composition that is currently used for HLW vitrification in the UK.

EXPERIMENTAL

A series of simplified simulated HLW glasses (based on the 4:1 HBU/MOX composition) were melted. The compositions are given in Table 1. The full simulated HLW glasses contain 25 elements but this composition was simplified in order to aid interpretation of results, and reduce

Table 1. Compositions of the glasses melted for this work.

Oxide	1%Mo glasses Weight %	Cs-Nd glasses Weight %	Cs-La glasses Weight %
SiO_2	61.18	45.92	45.92
B_2O_3	21.68	16.28	16.28
Na_2O	10.89	16.35	16.35
Li_2O	5.25	n/a	n/a
MoO_3	1.00	4.79	4.79
Cs_2O	n/a	3.11	3.11
Nd_2O_3	n/a	13.55	n/a
La_2O_3	n/a	n/a	13.55

the likelihood of interference from other elements on Mo related spectra. The 1%Mo glass is based on the MW glass frit used in the Waste Vitrification Plant at Sellafield doped with 1wt% Mo. The Cs-Nd and Cs-La glasses represent the same glass frit, although lithium oxide has been replaced by an equi-molar amount of sodium oxide to simplify analysis. The amounts of Cs and Nd/La have been boosted to account for the lack of other alkali metals and rare earths that would normally be found in the simulated HLW stream and the total amounts of Cs, Nd or La and Mo are representative of a 35wt% waste loaded glass. Reagent grade oxides or carbonates with purities ≥99.5% were used for the 100g glass batches, which were preheated to $1000^{o}C$ in alumina crucibles overnight to prevent thermal shocking of the crucibles upon insertion into the melting furnaces. The batches were then transferred to electric melting furnaces with Kanthal SiC elements and melted for a total time of 5.5hrs. After an initial 1 hour melt the samples were sparged with either O_2, compressed air or a $N_2/5\%H_2$ mix (depending on the oxidation/reduction conditions required) through pure alumina tubes inserted to approximately 10mm above the base of the crucible. The gas flow rate was 5 l/min. The glasses were then cast into steel block moulds, annealed at $550^{o}C$ for 1hr, and cooled to room temperature at $1^{o}C$/min.

Electron Spin Resonance and X-ray Photoelectron Spectroscopy experiments were performed to determine Mo oxidation states in the glass samples. For the ESR experiments, a 500g batch of the 1wt% Mo glass was melted for 5.5hrs at $1150^{o}C$ in a Pt crucible, and stirred with a Pt stirrer rotating at 60rpm for the last 4.5hrs of the melt. The glass was water quenched and then divided into 5 lots and remelted in alumina crucibles using the method described above. This was done to ensure the final samples for ESR were all derived from the same homogeneous precursor.

ESR samples were ball milled using alumina balls to a fine powder (<75μm) and were analysed using a Bruker ESP 300 spectrometer at a frequency of 9.89GHz at the University of Birmingham. XPS samples were cut into bars measuring 6 x 6 x 30mm and mounted in copper sample holders. The glasses were then fractured immediately prior to insertion in the spectrometer and analysed using a Scienta ESCA 300 at Daresbury Laboratories, with a pass energy of 150eV, slit width of 0.8mm and a take off angle of 45°. The number of scans acquired depended upon the concentration of Mo in the sample and the range of binding energies analysed. The data was corrected for the effect of sample charging by reference to O K_{α}.

RESULTS

1%Mo Glasses

Three 100g batches of 1%Mo glass from the original 500g precursor were re-melted and sparged with O_2, compressed air and N_2/5%H_2 respectively. The glasses melted in the oxidising and neutral atmospheres were both clear and colourless, consistent with the presence of Mo^{6+} (as Mo is the only species in the glass that should cause colouration), and the glass sparged with N_2/5%H_2 was a transparent smokey brown colour, which is indicative of the presence of Mo^{3+} [3]. The ESR spectra of the reduced glass (Fig.1) showed a strong resonance at $g = 1.9060(2)$, which again indicates the presence of Mo^{3+}, whereas the ESR of the oxidised and neutral melts (Fig.1, inset) showed only background noise which is consistent with the presence of Mo^{6+} in these glasses. However, upon melting another 100g batch of the 1%Mo glass under N_2/5%H_2 from the same precursor glass under the same conditions for XPS analysis, the resulting product was an opaque dark grey/black in colour. The XPS scan of this glass over the region of the main Mo binding energies (Fig.2) shows 2 main peaks at 232.2(1)eV and 235.2(1)eV which are caused by the Mo^{6+} 3d 5/2 and 3d 3/2 spin states respectively. The 3d 5/2 peak has a shoulder, the centre of which is at approximately 230eV which could indicate a trace of Mo^{4+} in this sample. According to Horneber [4], this is consistent with the colour of the sample if an iron-molybdenum redox couple is present. The ESR analysis of the black 1%Mo glass (Fig. 3) shows a resonance at $g = 1.908$, very similar to that seen in the brown 1%Mo glass, again indicating the presence of Mo^{3+}. However, the ESR technique is capable of detecting much smaller concentrations of a particular species than the XPS technique, and therefore this could explain why Mo^{3+} does not appear on the XPS scan.

The XPS scan of the 1%Mo glass melted in the air atmosphere (Fig.2) showed the two Mo^{6+} peaks and also exhibited a shoulder on the Mo^{6+} 3d 5/2 peak, possibly indicative of Mo^{4+}. However, the Mo^{4+} shoulder height/Mo^{6+} peak height ratio for the air sparged glass is significantly smaller than the Mo^{4+} shoulder height/Mo^{6+} peak height ratio for the reduced glass, which would suggest that there is less Mo^{4+} in the air sparged sample. Unfortunately, direct comparisons with absolute intensities cannot be made as the angle of cleavage of the sample surface with respect to the detector could not be measured.
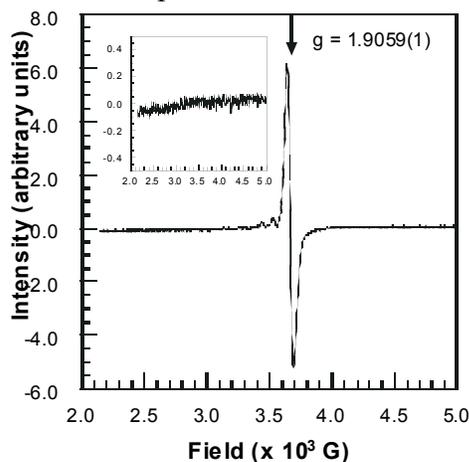

Fig. 1 : ESR of reduced 1%Mo glass
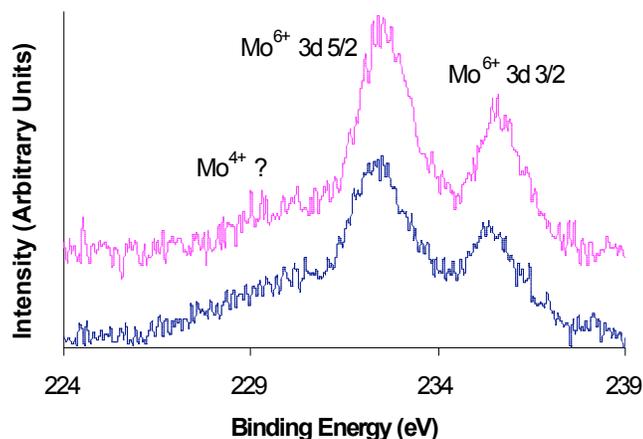Inset: ESR of air sparged 1%Mo glass

Fig. 2 : XPS of reduced 1%Mo glass (lower)
and air sparged 1%Mo glass (upper)

Cs-Nd Glasses

The Cs-Nd glasses melted with the oxidising and neutral sparges were both opaque violet coloured glasses. The violet colouration was caused by the presence Nd in these glasses. The glass melted in the reducing atmosphere was an opaque black colour, which is consistent with a reduction in the oxidation state of the Mo in this glass, as the violet colouration caused by Nd originates from the inner shell electron configuration and is therefore irrespective of the oxidation state of the Nd [5]. ESR analysis of these glasses showed that only the glass melted in the reducing atmosphere demonstrated a resonance at $g = 1.9059(2)$ (Fig.4) indicating the presence of Mo^{3+} in this glass.
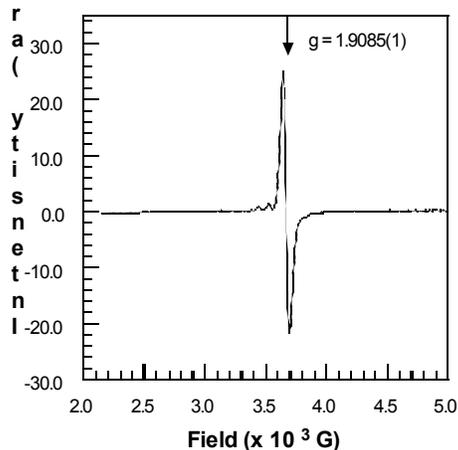

Fig. 3 : ESR of (black) reduced 1%Mo glass

Fig. 4 : ESR of reduced Cs -Nd glass

Cs-La Glasses

These glasses were produced as an analogue for the Cs-Nd glasses for the purposes of XPS, as it was noted that the Nd binding energies were likely to overlap with the Mo binding energies and further complicate the analysis. As the chemistry of La and Nd is very similar, little difference in the redox behaviour of Mo was expected in the Cs-Nd and Cs-La glasses. The Cs-Nd glasses sparged with O_2 and compressed air demonstrated no observable differences in characteristics so it was deemed unnecessary to produce an O_2 sparged Cs-La glass. The air sparged Cs-La glass was opaque and white in colour as compared with opaque black for the reduced Cs-La glass. The XPS analysis of the Mo region of the air sparged glass (Fig. 5) again showed the two Mo^{6+} peaks
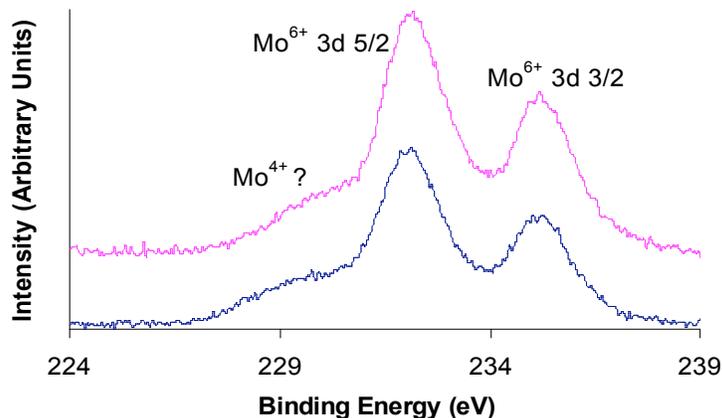

Fig. 5 : XPS of reduced Cs -La glass (lower) and air sparged Cs -La glass (upper)

at 232.0(1)eV and 235.0(1)eV. The signal to noise ratio of this scan compared to the 1%Mo glass scans suggest increased signal intensity, as would be expected from the greater concentration of Mo in this glass compared to the 1%Mo glasses. However, the shoulder at 230eV indicating the presence of Mo^{4+} which was seen in the reduced 1%Mo glass was also present in this scan. The scan of the same region for the reduced Cs-La glass (Fig. 5) showed the same characteristics as seen in the air sparged Cs-La glass, although the Mo^{4+} shoulder/Mo^{6+} peak height ratio was greater for the reduced glass indicating a larger amount of Mo^{4+} was present.

DISCUSSION

The ESR experiments on the 1%Mo glasses were based on experiments performed by Camara [3] and Horneber [4], who found that glasses containing Mo^{3+} gave resonances at $g = 1.906$. The ESR of both the brown and black 1%Mo glasses sparged with a reducing gas showed resonances in this region with $g = 1.9060(2)$ for the brown glass and $g = 1.9085(2)$ for the black glass, indicating the presence of Mo^{3+} in both glasses. The XPS results for the black glass showed the presence of Mo^{6+} and suggests the presence of Mo^{4+}, but no evidence of Mo^{3+}, indicating that the Mo^{3+} was not present in sufficient quantities in this glass to be detected by XPS. However, both glasses were melted from the same precursor material, and using identical experimental conditions. The colour difference indicates a qualitative difference between the two glasses, although the reason for this difference is at present unclear. It is possible that the black glass became contaminated at some point during the melting process, and colour differences were observed by Camara in similar glasses when small (<0.7mol%) iron additions were made to the batch [3]. However, the only contaminants that were observed on the XPS spectrum were fluorine, aluminium and carbon. F possibly arises from the HF acid used to clean the Pt crucible in which the original precursor batch was melted, Al from the alumina crucible used for melting and C collected on the fracture surface from the atmosphere prior to insertion into the spectrometer. No peaks were seen for Fe, or any other element likely to set up a redox couple with Mo, which could otherwise explain the colour difference between the two glasses. Another possible explanation is that the redox state of Mo is very sensitive to the oxygen partial pressure in the atmosphere. If this happened to be significantly different on the day of melting of the black glass, it could have changed the effect of the reducing atmosphere that the glass was being sparged with. Several repetitions have been performed of this melt using oxides and carbonates as batch materials (as opposed to the precursor batch used for the glasses discussed above) all of which have produced black glasses. Experiments are currently in progress to try to reproduce the brown glass (which, based on the work of Horneber [4] is the colour one would expect for a reduced glass containing small amounts of Mo^{3+}), using sugar as a reducing agent as well as sparging with a reducing gas.

The ESR results for the 1%Mo glasses melted in neutral and oxygen rich atmospheres were as expected and consistent with the presence of Mo^{6+} only in these glasses. However, the preliminary analysis of XPS data suggests the presence of Mo^{4+} in these glasses, although at a lower concentration than in the reduced 1%Mo glasses.

The ESR results obtained from the Cs-Nd glasses again showed that, as expected, Mo^{3+} was present in the glass melted in the reducing atmosphere and the glasses melted in the oxygen containing atmospheres were ESR silent, which is consistent with the presence of Mo^{6+} and the colour differences observed in these samples. However, the Cs-La glasses prepared under identical conditions to the Cs-Nd glasses suggested the presence of Mo^{4+} in both the reduced and

air-sparged samples. We have been unable to find any reference indicating an ESR resonance for Mo^{4+} and we suspect that it is ESR silent. Hence it is possible that it was present in the reduced Cs-Nd glass, but not identifiable via ESR. However, assuming the chemistry of Nd and La to be similar enough in these glasses to make the Cs-Nd glass results interchangeable with the Cs-La glass results, one can conclude that Mo^{4+} is likely to have been present in the air sparged Cs-Nd glass as its presence is indicated in the air sparged Cs-La glass. If this was the case and the air atmosphere allowed the reduction of Mo^{6+} (as it would be found in the MoO_3 used for the batch) to Mo^{4+}, one would also expect to see Mo^{5+} in the glass (as Mo^{5+} is a stable intermediate step between Mo^{6+} and Mo^{4+} [6]) which would have an ESR resonance. This was not the case. Again, it must be stressed that this is work in progress and that full analysis of the XPS data is not yet complete, but the results so far indicate that either the oxygen partial pressure is crucial in determining the extent of oxidation of the Mo, or that subtle differences in chemistry can have a major effect on the redox of Mo.

It was also noted from the wide scan of these glasses that the amount of Cs and Mo that had volatilised from the reduced Cs-La melt appeared to be greater than for the air sparged melt, as the corresponding peaks on the reduced glass wide scan were much less intense.

CONCLUSIONS

Small concentrations of Mo in simple alkali borosilicate glasses can be at least partially reduced from Mo^{6+} to Mo^{3+} by melting in a reducing atmosphere. The extent of this reduction appears to be sensitive to either small changes in pO_2 or small changes in glass chemistry. In similar glasses containing higher concentrations of Mo as well as rare earth ions, the reduction of Mo^{6+} to lower oxidation states appears to be possible even when melting in atmospheres abundant in oxygen.

ACKNOWLEDGEMENTS

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