

THE STRUCTURAL CHEMISTRY OF MOLYBDENUM IN MODEL HIGH LEVEL NUCLEAR WASTE GLASSES, INVESTIGATED BY MO K-EDGE X-RAY ABSORPTION SPECTROSCOPY

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ABSTRACT

The immobilisation of molybdenum in model UK high level nuclear waste glasses was investigated by X-ray Absorption Spectroscopy (XAS). Molybdenum K-edge XAS data were acquired from several inactive simulant high level nuclear waste glasses, including specimens of Magnox and Magnox / UO₂ waste glasses prepared during commissioning of the BNFL Sellafield Waste Vitrification Plant. These data demonstrate that molybdenum is immobilised in the Mo (VI) oxidation state as the tetrahedral MoO₄²⁻ species, with a Mo-O contact distance of *ca* 1.76 Å. The MoO₄²⁻ species are not immobilised within the polymeric borosilicate network, instead they are likely to be located in extra-framework cavities, together with network modifier cations. Molybdenum K-edge XAS data acquired from “yellow phase” material, removed from a sample of simulant Magnox waste glass, show that this substance incorporates Mo (VI), also present as tetrahedral MoO₄²⁻ species. The presence of isolated MoO₄²⁻ tetrahedra within the glass matrix provides an explanation for the initial rapid release of molybdenum from simulant HLW waste glasses in static dissolution experiments and the strong correlation of the initial Mo leach rate with that of Na and B.

INTRODUCTION

In the UK and France the highly radioactive fission products arising from the reprocessing of nuclear fuel are currently immobilised in an alkali borosilicate glass matrix. The fission products are classified as High Level nuclear Waste (HLW) due to their heat generating capacity. Alkali borosilicate glasses are the matrix of choice for the immobilisation of waste fission products since they show considerable flexibility with respect to chemical constitution, permitting vitrification of waste streams of variable composition [1, 2]. In addition, alkali borosilicate glasses may be

fabricated at reasonable temperatures, *ca* 1060°C, and show superior chemical durability with respect to other vitreous wasteforms (*e.g.* phosphate based glasses) [1, 2]. In Europe, vitrification of high level nuclear waste is currently undertaken at the Sellafield Waste Vitrification Plant (WVP), operated by British Nuclear Fuels plc, and the La Hague vitrification plants, R7 and T7, operated by COGEMA.

The incorporation of isotopes of molybdenum is of particular interest in the vitrification of HLW. This element is known to have a low solubility (≤ 1 wt% MoO₃) in borosilicate glass compositions and its presence in excess results in the phase separation of a complex yellow molten salt during vitrification [1]. The formation of so-called “yellow phase” material during the vitrification process is undesirable since this leads to accelerated corrosion of the (inconel) melter. Furthermore, this material, which is reported to contain other fission products (including ¹³⁷Cs), is soluble in aqueous solution providing a potential route for the facile dispersal of radionuclides [1].

In order to understand the role of molybdenum in the fabrication of HLW glasses we have undertaken a Mo K-edge X-ray Absorption Spectroscopy (XAS) study of a range of molybdenum bearing glasses, as listed in Table I. Molybdenum bearing alkali borosilicate glasses were prepared, as simple model analogues of the chemically complex simulant waste glasses, under mildly oxidizing or reducing conditions by sparging the glass melt with compressed air (Sample 1) or N₂ / H₂ (95 / 5 %, Sample 2), respectively. Samples of inactive simulant HLW glass produced during commissioning of the Sellafield Waste Vitrification Plant were provided by BNFL plc, two compositions were examined corresponding to vitrified HLW arising from the reprocessing of Magnox nuclear fuel (Sample 3) and a blend of HLW arising from the reprocessing of Magnox and UO₂ fuel (Sample 4); these glasses were formulated to achieve a HLW loading of *ca* 25 wt% in the glass matrix, on an oxides basis. Laboratory simulant glasses designed to approximate vitrified HLW derived from electro-dissolution of spent UO₂ fuel elements, as a future alternative to the current Purex reprocessing technology, were also studied. These glasses were formulated to achieve a HLW loading of *ca* 20 wt% in the glass matrix, on an oxides basis, and were fabricated under both mildly oxidizing and reducing conditions by sparging the glass melt with compressed air (Sample 5) or N₂ / H₂ (95 / 5 %, Sample 6). In addition, a specimen of “yellow phase” material recovered from a sample of full scale Magnox waste glass was analysed (Sample 7). The Mo K-edge XAS data show that in materials fabricated under both mildly oxidising and reducing conditions Mo (VI) is present as the tetrahedral MoO₄²⁻ species. Electron spin resonance data show that Mo (III) species are stabilised within the model and simulant HLW glasses fabricated under reducing conditions; however, Mo (VI) remains the dominant species.

EXPERIMENTAL

Sample preparation

CaMoO₄ and SrMoO₄. Samples of CaMoO₄ and SrMoO₄ were prepared by solid state reaction of stoichiometric quantities of MoO₃ and CaCO₃ or SrCO₃ at 800°C for 48h, in air. These materials were confirmed to be single phase by X-ray powder diffraction.

Laboratory simulants (Samples 1, 2, 5 and 6). Stoichiometric quantities of metal oxides or carbonates were intimately mixed, according to the desired batch composition, and heated in an alumina crucible, at 1 °C min⁻¹, to 1000 °C; the crucible was then transferred to a glass melting furnace at 1150 °C and allowed to equilibrate at this temperature for 1h. Subsequently, a high density alumina tube was inserted into the molten glass allowing compressed air or N₂ / H₂

(95 / 5 %) to be bubbled through the melt at a rate of *ca* 1 dm³ min⁻¹. The gas sparge allows the partial oxygen pressure in the melt to be varied and aids the formation of a homogeneous glass by continuously mixing the melt. The melts were sparged for 4.5 h at 1150 °C and then cast into rectangular blocks, annealed at 550 °C for 1 h and cooled to room temperature at 1 °C min⁻¹ in air. Ag was used as a surrogate for the noble metals Pd and Ru in Samples 5 and 6. X-ray powder diffraction revealed the presence of metallic silver in Sample 6, whereas Samples 1, 2 and 5 were not found to contain any significant amount of crystalline material.

Table I: Compositions of molybdenum bearing alkali borosilicate glasses studied by XAS; Samples 1 and 2 are simple “model” glasses; Samples 3 and 4 are specimens of full scale glasses designed to simulate vitrified Magnox / UO₂ and Magnox HLW, respectively; Samples 5 and 6 are laboratory glasses designed to simulate vitrified HLW arising from electro-dissolution of UO₂ fuel.

Component (wt %)	Sample					
	1	2*	3	4	5	6*
SiO ₂	61.18	61.18	46.10	46.28	49.44	49.44
B ₂ O ₃	21.68	21.68	15.90	15.9	17.52	17.52
Na ₂ O	10.89	10.89	8.29	8.59	8.80	8.80
Li ₂ O	5.25	5.25	4.07	3.92	4.24	4.24
Ag ₂ O	-	-	-	-	1.41	1.41
BaO	-	-	0.50	0.24	0.94	0.94
CeO ₂	-	-	0.84	1.86	1.33	1.33
Cs ₂ O	-	-	1.11	1.60	1.31	1.31
Gd ₂ O ₃	-	-	-	2.92	2.77	2.77
La ₂ O ₃	-	-	0.48	0.87	0.71	0.71
MoO ₃	1.00	1.00	1.62	2.21	2.39	2.39
Nd ₂ O ₃	-	-	1.44	2.77	3.00	3.00
Rb ₂ O	-	-	-	-	0.16	0.16
RuO ₂	-	-	0.70	1.03	1.49	1.49
Sm ₂ O ₃	-	-	0.22	0.44	0.44	0.44
SrO	-	-	0.30	0.55	0.41	0.41
TeO ₂	-	-	-	0.31	0.12	0.12
TiO ₂	-	-	0.01	0.06	0.53	0.53
Y ₂ O ₃	-	-	0.10	0.36	0.25	0.25
ZrO ₂	-	-	1.45	2.78	2.20	2.20
Fe ₂ O ₃	-	-	3.00	1.10	0.33	0.33
NiO	-	-	0.37	0.21	0.09	0.09
Cr ₂ O ₃	-	-	0.58	0.23	0.10	0.10
Al ₂ O ₃	-	-	6.58	1.59	-	-
CaO	-	-	0.01	0.03	-	-
MgO	-	-	5.74	1.41	-	-
K ₂ O	-	-	0.01	0.15	-	-
P ₂ O ₅	-	-	0.26	0.11	-	-
HfO ₂	-	-	0.02	0.06	-	-
Pr ₆ O ₁₁	-	-	0.44	0.85	-	-
Total	100.00	100.00	100.14	98.43	-	100.00

* Denotes glasses prepared using a N₂ / H₂ sparge.

Full scale simulants (Samples 3 and 4). Full scale inactive simulant HLW glasses were prepared during commissioning trials at the Waste Vitrification Plant, Sellafield, UK. In outline, a charge of sodium lithium borosilicate glass frit was added to the inconel melter (volume $\sim 0.12 \text{ m}^3$) and melted at *ca* 1080 °C with a compressed air sparge. Further frit, together with simulant high level nuclear waste material, was added to the melt over a period of hours to achieve the desired composition. The melt was allowed to homogenise over a period of 1h following the final addition of the simulant waste and frit, then discharged into a stainless steel canister (each canister holds $\sim 400 \text{ kg}$ of waste glass). Samples ($\sim 200 \text{ g}$) were randomly selected for study from the recovered material. X-ray powder diffraction revealed the presence of crystalline RuO_2 in the simulant Magnox and Magnox / UO_2 waste glasses (Samples 3 and 4, respectively).

“Yellow phase” material (Sample 7). An inclusion of “yellow phase” material, $\sim 0.1 \text{ g}$, was removed from a sample of full scale simulant Magnox waste glass by scraping with a spatula. This material was found to be composed of LiCsMoO_4 and other unidentified phases, by powder X-ray diffraction.

X-Ray Absorption Spectroscopy

Mo K-edge X-ray absorption spectra were collected on Station 16.5 at the Synchrotron Radiation Source, Daresbury, UK. The storage ring operates at 2 GeV with a typical beam current of 150 mA. A double crystal Si (220) monochromator was used, detuned to 50% of maximum intensity, for harmonic rejection. The Mo K absorption edge was calibrated by measuring the K-edge from a Mo foil at $E_0 = 19999.0 \text{ eV}$. Spectra were recorded at ambient temperature in transmission mode using ion chambers filled with a mixture of Ar (698 mbar) / balance He (incident beam, I_0) and Kr (368 mbar) / balance He (transmitted beam, I_t). The samples, in the form of fine powders, diluted where necessary with BN (in a *ca* 1:10 volume ratio), were packed into aluminium sample holders. At least two data sets were acquired per sample, over the energy range 19850 – 20850 eV. The spectral data were summed, calibrated and background subtracted using the programs EXCALIB, EXSPLINE and EXBACK. The background subtracted EXAFS data were analyzed using EXCURV98 [3], employing Rehr-Albers theory [4] and using single scattering. Phase shifts were derived from *ab initio* calculations using Hedin-Lundqvist potentials and von Barth ground states [5]. Theoretical fits were obtained by adding shells of backscattering atoms around the central absorber atom (Mo) and refining the Fermi energy, E_f , the absorber-scatterer distances, r , and the Debye – Waller factors, $2\sigma^2$, to minimize the sum of the squares of the residuals between the calculated and experimental EXAFS. The estimated precision in the refined absorber – scatterer contact distances is $\pm 0.02 \text{ \AA}$, the relative precision in the refined Debye – Waller factors is estimated to be $\pm 25 \%$. Shell occupancies, N_{occ} , were fixed at the integral values which gave the best fit as indicated by the EXAFS goodness of fit parameter, or R-factor, defined in reference 6.

RESULTS AND DISCUSSION

Mo K-edge XAS data were acquired from samples of CaMoO_4 and SrMoO_4 to provide a set of reference data for comparison with that acquired from the model and simulant HLW glasses. CaMoO_4 and SrMoO_4 crystallise in the Scheelite (CaWO_4) structure, with isolated MoO_4^{2-} tetrahedra [7]. The measured position of the Mo K-absorption edges in CaMoO_4 and SrMoO_4 , $E_0 = 20007.3 \text{ eV}$, is consistent with the presence of Mo (VI). The background subtracted EXAFS data from both samples were fitted with two co-ordination shells: an inner shell of four oxygen atoms at *ca* 1.75 Å and an outer shell of 8 Ca or Sr atoms at *ca* 4.0 Å. The crystal structures of

CaMoO₄ and SrMoO₄ are characterised by four equivalent Mo-O bond lengths and two distinct Mo-Ca/Sr contact distances to eight Ca/Sr near neighbours. For comparison, the Mo-O bond length and Mo-Ca/Sr contact distances for CaMoO₄ are, respectively, 4 x 1.757 Å, and 4 x 3.695 Å plus 4 x 3.402 Å; for SrMoO₄ the equivalent distances are 4 x 1.867 Å, and 4 x 3.814 Å plus 4 x 3.559 Å [7].

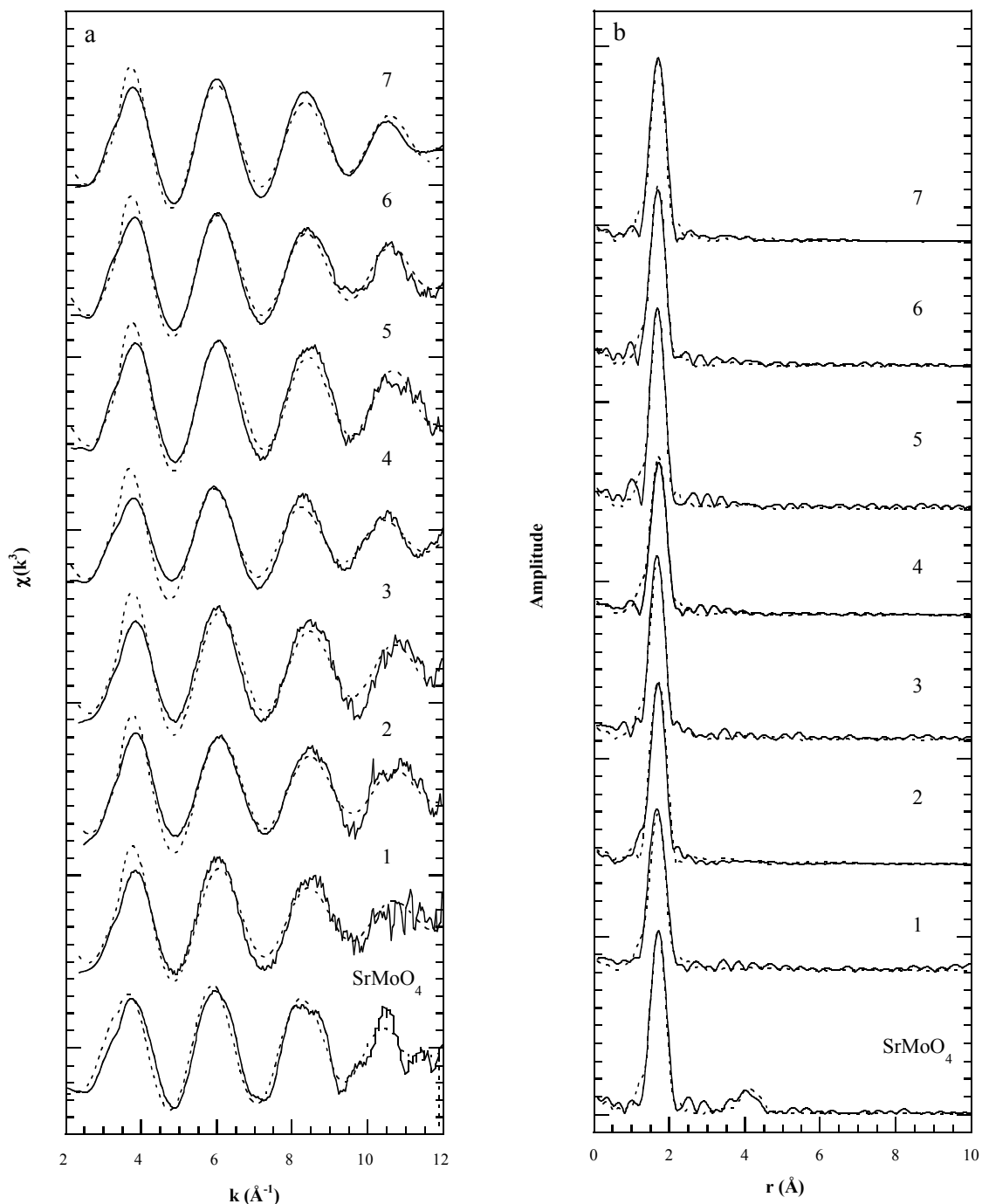


Figure 1: a) Experimental Mo K-edge EXAFS data (solid line) and model fit (broken line) for SrMoO₄, glass and "yellow phase" samples; b) corresponding radial distribution functions (see Introduction and Table I for sample identification).

The Mo-O contact distance for CaMoO₄ is in excellent agreement with the available crystallographic data for this compound. However, the Mo-O contact distance in SrMoO₄ is significantly longer than that determined by crystallographic methods. In both compounds the Mo-Ca and Mo-Sr contact distances are slightly larger than the average contact distance determined by crystallographic methods. The refined parameters are given in Table II and the background subtracted k³-weighted EXAFS spectrum and associated Fourier transform for SrMoO₄ are shown in Figure 2.

The position of the Mo K-absorption edge determined for the glass and “yellow phase” samples was not significantly different from that determined for the CaMoO₄ and SrMoO₄ reference materials, within the experimental precision of ± 0.5 eV, see Table III. The Mo K-edge X-ray Absorption Near Edge Structure (XANES) of the glass and “yellow phase” samples are also similar to those of the CaMoO₄ and SrMoO₄ reference material, as demonstrated by Figure 2. These observations indicated that in these materials the oxidation state and speciation of molybdenum were essentially identical, *viz.* Mo (VI) present as isolated MoO₄²⁻ species.

The background subtracted EXAFS from all glass samples and the “yellow phase” material were adequately fitted with a single co-ordination shell of four oxygen atoms at a distance of *ca* 1.76 Å from the central molybdenum absorber atom. The refined parameters are given in Table III and the background subtracted k³-weighted EXAFS spectra and associated Fourier transforms are shown in Figure 1. The average Mo-O contact distance of 1.76 Å is consistent with the Mo-O bond length observed in isolated tetrahedral MoO₄²⁻ species; for example, the five different MoO₄ tetrahedra in La₂(MoO₄)₃ and Ce₆(MoO₄)₈(Mo₂O₇) have average Mo-O bond lengths of 1.78 Å and 1.76 Å, respectively [8]. These data are also consistent with Mo K-edge XAS studies of molybdenum bearing Na₂O-K₂O-SiO₂ glasses in which an average Mo-O contact distance of 1.77 Å was determined [9].

Table II: Refined parameters for fit to XAS data for CaMoO₄ and SrMoO₄.

Sample	E ₀ (eV)	Shell	Type	N _{occ}	r (Å)	2σ ² (Å ²)	2σ _{Mo} ² (Å ²)	R
CaMoO ₄	20007.3	1	O	4	1.76	0.007	0.010	24.49
		2	Ca	8	4.16	0.028		
SrMoO ₄	20007.3	1	O	4	1.74	0.009	0.010	22.51
		2	Sr	8	4.08	0.018		

Table III: Refined parameters for fit to EXAFS data for glass and “yellow phase” samples, (see Introduction and Table I for sample identification).

Sample	E ₀ (eV)	Shell	Type	N _{occ}	r (Å)	2σ _{Mo} ² (Å ²)	2σ _O ² (Å ²)	R
1	20007.5	1	O	4	1.74	0.010	0.013	36.7
2	20007.5	1	O	4	1.74	0.010	0.012	29.7
3	20007.3	1	O	4	1.78	0.010	0.012	30.2
4	20007.5	1	O	4	1.74	0.010	0.010	36.1
5	20007.5	1	O	4	1.76	0.010	0.009	19.0
6	20007.4	1	O	4	1.78	0.010	0.010	34.0
7	20007.4	1	O	4	1.77	0.010	0.005	26.2

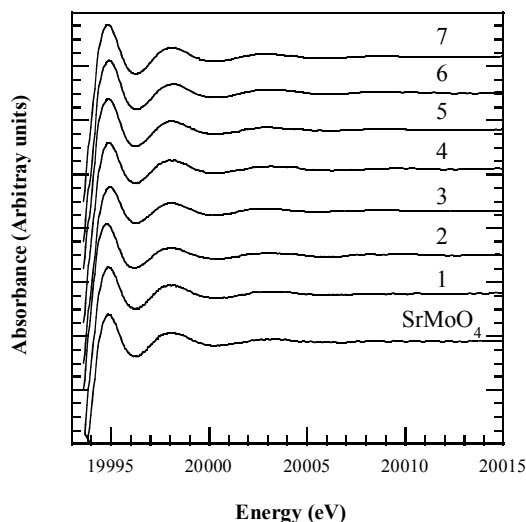


Figure 2: Mo K-edge XANES for SrMoO₄, glass and “yellow phase” samples, (see Introduction and Table I for sample identification).

The EXAFS and XANES data presented here show that Mo (VI) is present as the MoO₄²⁻ species in both simple model alkali borosilicate glasses and the more chemically complex simulant HLW glasses. Since only one co-ordination shell was required to adequately fit the EXAFS data and the corresponding Fourier transforms show no significant peaks (corresponding to potential next nearest neighbour Si atoms) at contact distances greater than 1.76 Å we infer that the MoO₄²⁻ species do not form part of the polymeric network in these materials. Instead, these MoO₄²⁻ species are likely to be encapsulated, together with network modifier cations, within cavities defined by the borosilicate glass network. This conclusion is in agreement with the model proposed by Calas *et al.*, based on molecular dynamics simulations and a Mo K-edge XAS study of the French SON68 simulant HLW glass [10].

The presence of isolated MoO₄²⁻ species within cavities defined by the polymeric glass network raises pertinent questions with respect to leaching of molybdenum from (simulant) HLW glasses. In the general model for glass corrosion in aqueous solution, network hydrolysis precedes network dissolution and the release of alkali metals, followed by the precipitation of secondary alteration products as leached species reach solubility limited concentrations. Thus, on the basis of a model of isolated MoO₄²⁻ species encapsulated within cavities formed by the polymeric glass network, the rate of release of Mo, Na and B (a tracer for network dissolution) would be expected to be closely correlated. Indeed, static leach test data from simulant Magnox waste glasses indicate the initial leach rates of Na, B and Mo to be essentially equivalent [11].

X-band Electron Spin Resonance (ESR) spectra acquired at room temperature from the glasses fabricated under reducing conditions (Samples 2 and 6) show a sharp resonance centered at $g = 1.9060(1)$, see Figure 3. This is consistent with the ESR data acquired from reduced molybdenum bearing silicate glasses studied by Camara *et al.* and Horneber *et al.*, and is attributed to Mo (III) species trapped within the alkali borosilicate glass matrix [12, 13]. In contrast, the ESR spectra acquired from glasses fabricated under mildly oxidising conditions were silent (Sample 1) or were characterised by a broad signal associated with paramagnetic transition metal species (Samples 3, 4 and 5), see Figure 3b. These data confirm that reducing conditions are indeed effective in stabilising Mo (III) species within these glasses, however, the

position of the Mo K-absorption edge in the XAS spectra of these glasses, 20007 eV, demonstrates that Mo (VI) is the dominant species. Spin counts acquired using a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ standard indicated that approximately 1.6 % of the total molybdenum in Sample 2 is present as reduced Mo (III) species.

It has been suggested that reducing the oxidation state of molybdenum may increase the solubility of this element in HLW waste glasses [1], thereby inhibiting the formation of the “yellow phase” molten salt during vitrification thus reducing the rate of melter corrosion. The data presented here confirm that reduced Mo (III) species may be stabilised in such glasses, although at low concentration. It is anticipated, however, that a reducing environment may result in the precipitation of noble metals from the glass, as indicated by the observation of metallic silver in Sample 6, prepared under reducing conditions. This is undesirable since noble metal precipitates are known to form a viscous “heel” at the bottom of the melter which may lead to blockage of the drain during discharge. Therefore, there would appear to be little incentive to fabricate HLW glasses under a reducing atmosphere in an effort to increase the incorporation of molybdenum.

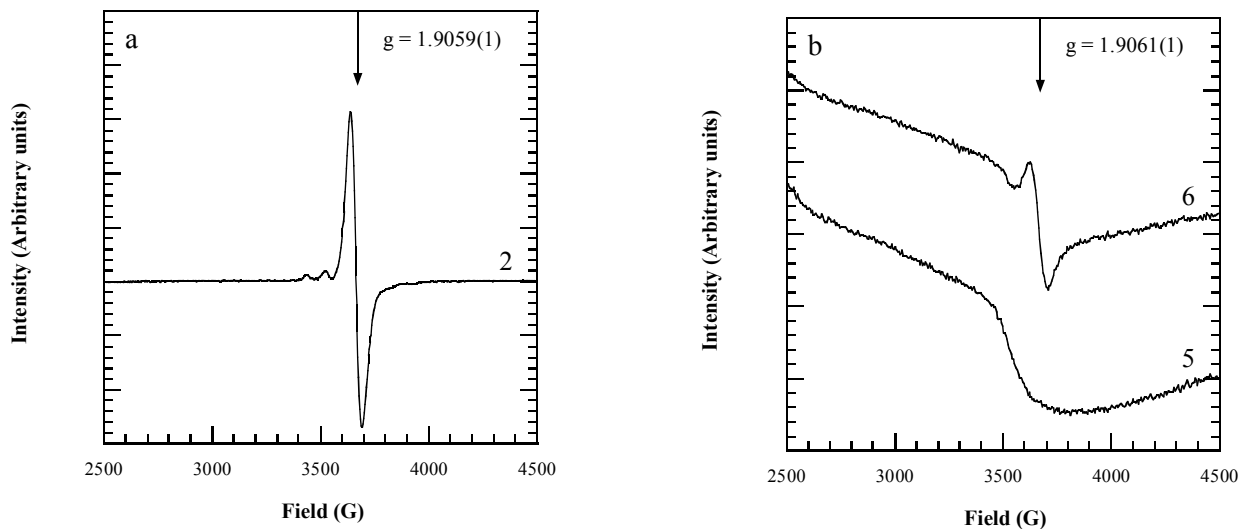


Figure 3: Electron spin resonance data from a) Sample 2 and b) Samples 5 and 6, showing a sharp resonance attributed to Mo (III) species in glasses fabricated under reducing conditions (Samples 2 and 5; see Introduction and Table I for sample identification).

CONCLUSIONS

Analysis of Mo K-edge XAS data has shown that Mo (VI) is present as isolated, tetrahedral, MoO_4^{2-} species in alkali borosilicate glasses and recovered “yellow phase” material. Electron Spin Resonance data confirm that reducing conditions allow the stabilisation of Mo (III) species within the glass melt, although at low concentration and Mo (VI) remains the dominant species. The presence of isolated MoO_4^{2-} tetrahedra within the glass matrix provides an explanation for the initial rapid release of molybdenum from simulant HLW waste glasses in static dissolution experiments and the strong correlation of the initial Mo leach rate with that of Na and B.

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