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Leaching behaviour of and Cs disposition in a UMo powellite glass–ceramic

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ABSTRACT

A UMo powellite glass–ceramic designed by French workers to immobilise Mo-rich intermediate-level waste was found to be quite leach resistant in water at 90 °C with the dissolution of Cs, Mo, Na, B and Ca not exceeding 2 g/L in normalised PCT tests. ¹³³Cs solid state nuclear magnetic resonance and scanning electron microscopy (SEM) showed the Cs to inhabit the glass phase. The microstructures were not greatly affected by cooling rates between 1 and 5 °C/min or by introducing 10 times as much Cs and Sr. Protracted leach tests at 90 °C showed surface alteration as evidenced by SEM and particularly transmission electron microscopy; the main alteration phase was a Zn aluminosilicate but several other alteration phases were evident. Voidage in the alteration layers was indicated from enhanced lifetimes in positron annihilation lifetime spectroscopy.

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1. Introduction

Waste from reprocessed UMo nuclear fuel is rich in Mo, so a new UMo glass–ceramic formulation was devised by CEA scientists to accommodate ~10 wt% of Mo [1,2] as well as a few percent of fission products. The short-term leachability as measured by Soxhlet testing is ~3 g/m²/day [3]. PCT-type testing at 90 °C using a glass surface area–water volume ratio of 80 cm^{−1} gave a B leach rate of 2.5×10^{-6} g/cm²/day over the 91–120 day leach period [3]. However since when Mo is present, Cs in glasses can sometimes form water-soluble Cs molybdate, we have focussed on the disposition of Cs by solid state nuclear magnetic resonance and scanning electron microscopy and the leachability of Cs in the UMo glass–ceramic.

Leaching in deionised water at 90 °C was studied by elemental extraction in PCT tests [4] and surface alteration methods. These latter methods included glancing angle X-ray diffraction, scanning and transmission electron microscopy and positron annihilation lifetime spectroscopy. The resistance to leaching offered by alteration layers will depend partly on their porosity. Positrons injected into dense solids typically have lifetimes of 0.1–0.2 ns before they annihilate with electrons, but the presence of nanovoids

gives rise to longer lifetimes because of the reduced electron density in such voids.

2. Experimental

The UMo glass–ceramic composition employed was (wt%): Na₂O (9.3); B₂O₃ (14.2); Al₂O₃ (7.0); MoO₃ (9.9); P₂O₅ (3.0); ZnO (5.9); ZrO₂ (3.3); CaO (6.1); Cs₂O (0.3); SrO (0.4); Nd₂O₃ (1.7); SiO₂ (38.9). This was very similar to an earlier French composition [1]. Na, Al, Zn, Ca, Cs, Sr, and Nd nitrates were dissolved in water, the P was added as (NH₄)₂HPO₄, the Mo, Zr and B as dry metal oxides and the Si was added as Ludox, a 50 wt% aqueous colloidal solution. The mixture was stir-dried and calcined in air at 750 °C for 1 h before ~15 g samples were melted in Pt crucibles at 1280 °C for 1 h using thermal ramp rates of 5 °C/min for heating and 5 °C/min or 1 °C/min cooling rates. Sample density was determined to be 2.71 g/cm³ using Archimedes' method in distilled water.

X-ray diffraction patterns were measured using a Philips PW1050 diffractometer (PANalytical Ltd., Almelo, Netherlands) with Cu K α radiation. Grazing incidence X-ray diffraction (GI XRD) measurements were performed using a BRUKER D8 Advance diffractometer, utilizing Cu K α radiation and a SOL-XE energy dispersive detector with a step size of 0.03° and a counting time of 20 s per step. The diffractometer was fitted with an incident beam Göbel mirror and 0.18 parallel-plate collimator for parallel beam

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conditions. The incident angle was set at 1, 2 or 3° to achieve a maximum extinction of X-rays between 1–3 μm from the surface. Scanning electron microscopy was carried out with a Zeiss Ultra Plus instrument operating at 15 kV and equipped with an Oxford Instruments X-Max 80 mm² SDD X-ray microanalysis system for semi-quantitative phase-composition analysis. Samples were mounted in epoxy resin and polished to a 1 μm diamond finish. A ~5 nm thick carbon film was deposited on the surface to remove charging effects.

High-resolution solid-state NMR experiments were carried out on a 9.4 T Varian Infinity (CMX) spectrometer operating at a Larmor frequency of 52.48 MHz for ¹³³Cs. Samples were packed in 4 mm zirconia rotors and spun at 15 kHz. The crystalline spectra were acquired with a simple Bloch decay ($\pi/18$) with a pulse repetition rate of 200 s, which were non-saturating conditions and the glasses with $\pi/2$ solid-echo with an exorcycle phase scheme. The time domain data were zero-filled to $t = 0$ before Fourier transformation to eliminate any phase distortion of spinning sidebands. Spectra were referenced to aqueous 1 M CsCl via a secondary reference to solid CsCl.

Transmission electron microscopy (TEM) was performed using a JEOL JEM 2010F (JEOL, Japan) equipped with a field emission gun (FEG) electron source operated at 200 kV. The TEM was equipped with an energy dispersive X-ray (EDX) spectrometer and NORAN System SIX microanalysis system (Thermo Electron Corporation, USA). The TEM specimen was prepared by lightly scraping the surface of the leached monolith to remove some of the leach product which was then lightly ground under ethanol and a few drops of the suspension deposited onto a holey carbon coated copper TEM grid.

7-day leaching experiments at 90 °C were conducted in triplicate on PCT powder samples. A hand ground sample of the glass ceramic was passed through a 150 μm mesh sieve, followed by a 75 μm mesh sieve. The 75–150 μm glass ceramic powder was ultrasonically cleaned 3 times in cyclohexane, at 5 min intervals, to remove adhering fines. The cleaned sample was placed in an oven at 90 °C to dry then cooled to room temperature.

All tests were carried out in triplicate in clean Teflon vessels. Parallel blank tests, in duplicate, were also carried out to provide background levels of constituent elements. To each sample, ASTM Type 1 water was added at the ratio of 10 mL per 1 g of sample mass. The pH and temperature of the ASTM Type 1 water were measured using a calibrated Metrohm 713 pH meter. The set of samples, including the blanks, was placed immediately into a calibrated, preheated oven at 90 °C and leached for 7 days.

After 7 days of leaching the samples were removed from the oven. As soon as the leachate had cooled to ambient temperature the vessels were reweighed and the sample filtered. Using a 0.45 μm Sartorius Minisart filter attached to a 20 mL Terumo syringe, the filtered leachates were poured into clean, pre-weighed, labelled 25 mL polyethylene containers. A 5 mL aliquot of leachate was transferred into a clean labelled 25 mL polyethylene container for the pH measurement. The pH and temperature of the aliquot were measured using a calibrated Metrohm 713 pH meter. The leachates were acidified with Tracepur[®] HNO₃ equal to 3% of the leachate volume. The acidified leachates and blanks were submitted for ICP-MS and ICP-OES analysis to quantify the cations present in each leachate.

The leachates were analysed for Mo and Cs using a Varian 820-MS system equipped with nickel cones, Micromist low flow nebuliser, double-glass Scott spray chamber, and SPS3 autosampler. The leachate was analysed for Na, Ca, and B using a Perkin Elmer Optima 5300DV ICP-OES system equipped a Rytan, double-pass Scott-type spray chamber, a GemTip Cross-Flow pneumatic nebuliser and a CETACC520 autosampler.

More extended leach tests were conducted on groups of three 6 × 6 × 2 mm plates of material which were polished to a 1 μm diamond finish on one large face and were all immersed in 100 mL of deionised water at 90 °C for various times and then individual plates were studied by glancing incidence X-ray diffraction, scanning electron microscopy or positron annihilation lifetime spectroscopy. Solution analysis was carried out as above. X-ray fluorescence data were obtained on a Rigaku WDXRF “Primus II” spectrometer with a Rh tube, using pressed pellets of powdered glass-ceramics and analysed with a semi-quantitative standard-less SQX program.

Positron annihilation lifetime spectroscopy on leached glass-ceramic surfaces was mainly studied using the beamline [5] at the Australian National University in which pulsed positrons having energies of 1–20 keV and ranges in the solids of up to ~1 μm can be utilised. Positrons injected into dense solids typically have lifetimes of 0.1–0.2 nsec when they annihilate with electrons, but the presence of nanovoids gives rise to longer lifetimes, as positrons become trapped in the voids where there is a near absence of electrons. The apparatus utilises a ²²Na source moderated by solid Ne combined with a Surko trap to produce a pulsed beam of variable energy positrons, 5 keV in the present case, giving a mean penetration depth of approximately 200 nm. Annihilation gammas are detected after injection into the sample using a BaF₂ crystal combined with a fast photomultiplier tube. The pulses typically have ~800 ps full width at half maximum (FWHM). The shortest lifetime able to be confidently resolved by the positron beam is ~0.3 ns after an accumulation of 1.5 million counts.

A benchtop PALS setup was also employed to study the bulk properties of the glass-ceramics, with sandwiches of solids ~10 mm square or in diameter and about 3 mm thick, with the large faces adjacent to the positron source polished to a 1 μm diamond finish. The arrangement of an 8 μm thick kapton sandwich containing ~30 μCi of ²²NaCl as described by Guagliardo et al. [6] using similar electronic gamma detection was used to obtain the PALS spectrum of the unleached solids, to assist defining the beamline PALS results as representative of the alteration layers or the bulk material. Here over 10⁶ counts were accumulated and measurements were conducted at room temperature and in air. The spectra were deconvoluted using PALSFIT Version 1-64 software [7] to obtain the various lifetime components. The average experimental errors are of the order of 2 ps for the lifetime results and <1% for the intensities.

3. Results and discussion

While Schuller et al. [2] concentrated on phase separation phenomena in similar glass-ceramics which were quenched from the melt, our focus is a material poured from the melt into canisters. Such material would have cooled relatively slowly and 5 °C/min is doubtless an overestimate of the cooling rate, but will be a lot more realistic than quenching. The materials were partly translucent and X-ray diffraction (Fig. 1) showed the principal crystalline species present was CaMoO₄ (JCPDS card 29-351), with a minor apatite phase containing Nd (JCPDS card 32-175), plus a glassy phase giving rise to a diffuse hump centred at around 25° in 2 θ .

SEM results for this glass are shown in Fig. 2(a) and (b), in which the samples were cooled from the melt at 5 and 1 °C/min respectively. As found by previous workers [2] the phase-separated regions constitute around 15% of the sample volume. The white regions in the phase separated globules are basically CaMoO₄ containing the Sr, some of the Zn and most of the Nd presumably substituting for Ca, plus a small amount of glass; the grey regions of the globules are apatites containing Zn and Nd; and the

Fig. 1. XRD pattern from UMo glass–ceramic. Diffuse peak between ~ 15 and 40° of 2θ due to glass. The main peaks derive from powellite, CaMoO_4 (JCPDS29-351).

Fig. 2. Backscattered SEM of UMo glass–ceramic cooled from the melt at (a) $5^\circ\text{C}/\text{min}$ and (b) $1^\circ\text{C}/\text{min}$ and (c) the glass–ceramic containing 10 times more Cs and Sr, cooled at $5^\circ\text{C}/\text{min}$ from the melt.

aluminosilicate glass matrix is devoid of phosphate, but contains around 20% of the Mo. XRF results confirmed the final composition of the glass–ceramics was very close to the starting stoichiometry.

XRF showed the composition of the glass–ceramic cooled at $1^\circ\text{C}/\text{min}$ was essentially unaltered by the change of heat treatment, apart possibly from a small loss of Na because of the extended time above the melting point. XRD gave similar results to that for the material cooled at $5^\circ\text{C}/\text{min}$. The phase separation details were slightly altered insofar as the globules exhibited a finer structure (see Fig. 2(b)) and the glass composition was basically the same. In another sample in which the contents of Cs and Sr were increased to 10 times that of the above material, the phase separation structure was substantially unaltered (Fig. 2(c)).

3.1. ^{133}Cs MASNMR spectroscopy

The ^{133}Cs MASNMR spectra can give an element specific view of the location of Cs in the phase separated UMo glass–ceramic in either crystalline or glassy fractions. Central transition ^{133}Cs MASNMR spectra in well-ordered crystalline Cs aluminosilicate phases have shown quite narrow resonance lines [8] due to the low nuclear quadrupole moment of the ^{133}Cs nucleus ($-3.4 \times 10^{-31} \text{ m}^2$) and the absence of broadening of the central ($\pm m_1 = 1/2$ transition), by the first order quadrupole effect. The spectrum shown in Fig. 3(a) is of pure caesium molybdate (Cs_2MoO_4). In addition to narrow lines this crystalline sample also exhibits a long spin–lattice relaxation time and requires long acquisition times. The spectrum shown in Fig. 3(b) was acquired with an echo, but with relaxation characteristics that would allow the observation of Cs in a crystalline phase. The large ^{133}Cs line width of the UMo glass spectrum is attributed to a wide distribution of chemical shifts resulting from a distribution of bond-lengths and angles typical of a glass. In Fig. 3(c) the ^{133}Cs MASNMR spectrum of the widely known SON68 surrogate glass for the R7T7 nuclear waste glass is shown for comparison and shows a similar spectral response.

3.2. Durability assessment

PCT results at 90°C for the glass–ceramics cooled from the melt at 1°C and $5^\circ\text{C}/\text{min}$ are shown in Table 1. Although they showed higher leach rates for Ca and Mo for the $5^\circ\text{C}/\text{min}$ cooling rate, as

Fig. 3. ^{133}Cs MAS NMR spectra of (c) crystalline Cs_2MoO_4 , 16 scans (Bloch decays) $\pi/18$ pulses with 1000 s delay; (b) UMo glass obtained with 287 scans (echoes) and 200 s delay spun at 15 kHz; (a) SON68 glass, obtained with 105000 scans (echoes) with 0.5 s delay spun at 13 kHz.

Table 1

Normalised PCT results for various elements in glass–ceramic cooled from the melt at nominal rates of 1 and 5 °C/min.

Element (g/L)	Cooling rate (°C/min)	
	1	5
Na	1.9	1.7
B	2.0	1.2
Cs	0.3	0.4
Mo	0.7	1.2
Ca	0.03	0.6

against the 1 °C/min cooling rate, all measured values were reasonably low, $<0.2 \text{ g/m}^2/\text{d}$.

$6 \times 6 \times 2 \text{ mm}$ -sized plates of glass–ceramic, polished down to $1 \mu\text{m}$ diamond on one side, were leached in a large volume of water for 1 or 3 months. The derived Na, B, Si, Cs, Mo, and Al normalised leach rates of the sample cooled from the melt at 5 °C/min for 90 days' exposure all corresponded to $0.2 \text{ g m}^{-2} \text{ day}^{-1}$ within a factor of two.

Although there were visual indications of a thin alteration layer after leaching, no crystalline alteration phases were observed from glancing angle XRD. SEM showed evidence of the alteration layer insofar as the images appeared blurred, but chemical information on its nature could not be obtained.

From TEM, a sheet like Zn–Al–Si–O phase formed the bulk of material collected from the leached sample (Fig. 4(a)). Selected area electron diffraction (SAED) shows a fine-grained polycrystalline structure (Fig. 4(b)). A very fine-grained Zr–Si–Al–O phase was also common (Fig. 5(a)) which selected area electron diffraction showed to be amorphous (Fig. 5(b)). Several minor

Fig. 5. (a) Elemental analysis using TEM–EDS and (b) SAED for the Zr–Si–Al–O phase.

Zr–Nd–Zn–Ca–P–O crystalline phases with different morphology were also present in the alteration products. Examples of these are shown in Fig. 6.

3.3. PALS measurements

To our knowledge, no previous PALS work has been carried out on nuclear waste glasses or glass–ceramics and we are starting such work at ANSTO. PALS measurements of the bulk properties of the unleached glass–ceramic cooled at 5 °C/min from the melt gave a main ($\sim 80\%$) lifetime at 0.35 ns and a minor ($\sim 20\%$) lifetime component at 0.87 ns, using the benchtop equipment. Results from the beam-based PALS on the leached surface of the glass–ceramic for a range of leaching times are given in Table 2. The results for the unleached sample were somewhat different to that from the benchtop measurements, particularly in regard to the intensity and lifetime of the minor second lifetime component. This is perhaps due to the enhanced surface sensitivity of the beam experiment, and may be due to polishing strains. Note that the intensities from the beam-based data do not add to 100% as only lifetimes that are different from those present in a reference sample are reported. For the 43 day leached sample, we see an increase in the shortest lifetime observed, along with lifetimes of 6 and 66 ns, corresponding to pore radii of 0.5 and 5 nm respectively, using the extended Tau–Eldrup model [9]. The shorter lifetimes observed in the measurements are not so easily related to pore sizes, and probably correspond to vacancy clusters of a few atoms within the alteration layers, with increasing lifetimes indicating increasing size. In the case of the 90 day leached sample, the shortest

Fig. 4. (a) Elemental analysis using TEM–EDS and (b) SAED for the Zn–Al–Si–O phase.

Fig. 6. TEM images for various minor Zr–Nd–Zn–Ca–P–O crystalline phases.

Table 2

Beamline positron lifetimes for 90 °C leached glass–ceramic cooled from the melt at 5 °C/min.

Time (days)	τ_1 (ns)	I_1 (%)	r_1 (nm)	τ_2 (ns)	I_2 (%)	r_2 (nm)	τ_3 (ns)	I_3 (%)	r_3 (nm)
0	0.34	41		1	4				
43	0.56	28		6	5	0.5	66	8	5
90	0.76	25		39	1.5	1.2			

lifetime component increases again, and a single long lifetime of 39 ns is observed, corresponding to a pore radius of 1.2 nm.

It would seem that as the more leachable ions are removed from the glass, they leave behind vacancy clusters of increasing size, corresponding to the short lifetime components observed. The longer lifetime components indicate the formation of open-volume defects in the surface alteration layer(s) of the glass. Over time, the size of these channels or voids can change and the reduced intensity component of the long lifetime observed in the 90 day leached sample indicates that these defects may even be closing over time, as the alteration layer as a whole thickens.

4. Conclusions

The phase separation details in the French UMo powellite glass–ceramic were only slightly affected using different cooling rates of a few °C/min and canisterised material produced from melts should be appropriately leach resistant at 90 °C insofar as the normalised leaching of all elements studied did not exceed 2 g/L in a 7-day PCT test. The 90 day leach rates in more dilute aqueous solutions were around 0.2 g m^{−2} day. All the Cs appears to be in the glass phase as shown by NMR and SEM and the Sr is in solid solution with the CaMoO₄ phase. Extended leaching at 90 °C gave rise to a variety of alteration phases as observed by transmission electron microscopy and indications in positron annihilation lifetime beam spectroscopy of open volume defects such as voids or channels in the altered layer. It is of course recognised that drying and

evacuation could have some effects on the overall porosity of the alteration layers.

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