Crystallisation of Magnox waste glass under conditions of high temperature, very deep, geological disposal

N. C. Hyatt,[1] *K. J. Taylor, F. G. F. Gibb & W. E. Lee*

Immobilisation Science Laboratory, Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK

The behaviour of a simulant Magnox waste glass was investigated under the likely conditions of high temperature, very deep, geological disposal, namely 760°C and 0·15GPa, to assess the suitability of this scheme for disposal of high level vitrified nuclear waste. Partial crystallisation of the glass is observed under these conditions with the formation of $LnBSiO_5$ (Ln=Y, La, Pr, Ce, Nd, Sm and Gd), $LiNaZr_6SiO_{15}$ and a palladium (ruthenium) telluride phase. We conclude that, in principle, the partial crystallisation of Magnox waste glass under these conditions presents no impediment to the very deep, high temperature, geological disposal of vitrified high level nuclear waste.

High temperature, very deep, geological disposal is an alternative to the conventional mined repository concept for the disposal of high level nuclear waste (HLW).[1,2] In this scheme, a large diameter borehole is drilled into suitable rock (e.g. granite) to depths in excess of 4 km, subsequently HLW packages are lowered into the borehole which is then backfilled with host rock and sealed. The primary requirement of the HLW package is to provide sufficient energy to heat the waste package and the surrounding rock to 800–900°C at the required depth. This results in partial melting of the host rock which, subsequently, recrystallises as the thermal output of the HLW material diminishes over time, sealing the HLW packages in an envelope of durable mineral phases. Any fractures in the rock surrounding the HLW packages are sealed by recrystallisation, annealing or hydration reactions, preventing the access of hydrous fluids to the HLW packages. Furthermore, at depths of several kilometres, hydrous fluids are physically and chemically isolated from near surface groundwaters, effectively inhibiting transport of radionuclides to the biosphere. This scheme maximises the geological barrier between the HLW material and the biosphere, in contrast to the mined repository concept which, by comparison, is geologically shallow. Since the geological barrier is the only barrier which can be assured over the required timescale for HLW disposal (>10^6 years) the high temperature, very deep, disposal scheme presents an inherently safer alternative to conventional repository disposal concept. The thermal budget of the HLW packages may be optimised in a number of ways, including co-disposal of spent nuclear fuel and vitrified high level waste material. In order to assess the suitability of the very deep, high temperature, disposal strategy for such a co-disposal scenario, it is necessary to examine the behaviour of high level waste glasses and spent fuel material under such conditions. Accordingly, we have investigated the behaviour of a simulant Magnox high level waste glass, with the composition in Table 1, under likely conditions of high temperature, very deep, geological disposal, namely 760°C and 0·15 GPa.

Table 1. *Composition of the simulant Magnox waste glass employed in this study. Note, this analysis did not include an assay of palladium or tellurium*

Component	*wt%*	*Component*	*wt%*	*Component*	*wt%*	*Component*	*wt%*
SiO_2	46·1	MoO_3	1·62	BaO	0·50	Y_2O_3	0·10
B_2O_3	15·9	ZrO_2	1·45	La_2O_3	0·48	HfO_2	0·02
Na_2O	8·29	Nd_2O_3	1·44	Pr_6O_{11}	0·44	TiO_2	0·01
Al_2O_3	6·58	Cs_2O	1·11	NiO	0·37	CaO	0·01
MgO	5·74	CeO_2	0·84	SrO	0·3	K_2O	0·01
Li_2O	4·07	RuO_2	0·70	P_2O_5	0·26		
Fe_2O_3	3·00	Cr_2O_3	0·58	Sm_2O_3	0·22		

Experimental

The heat treatment of Magnox waste glass was undertaken using the general experimental procedure described by Attrill & Gibb.[3] A core drilled specimen of Magnox waste glass was placed in a gold capsule, together with 2 wt% of distilled water to maintain the pressure inside the capsule and simulate the effect of water trapped within the HLW container (which could conceivably arise during manufacture, storage or disposal). The capsule was crimped and welded shut using a carbon arc microwelder. Retention of water was

[1] Corresponding author. Email: n.c.hyatt@sheffield.ac.uk

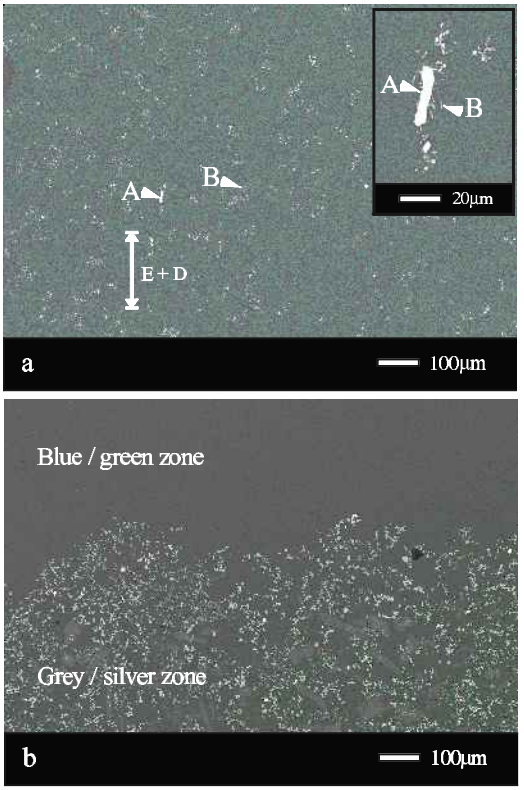

Figure 1. *Back scattered electron images of (a) initial and (b) heat treated simulant Magnox waste glass (axial cross section); A and B denote palladium telluride and RuO_2 phases, respectively. The inset shows the region around 'A' in Figure 1(a) at higher magnification*

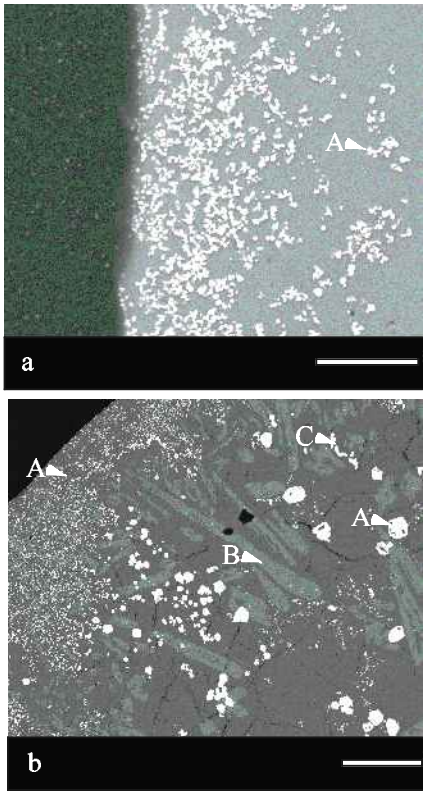

Figure 2. *Back scattered electron images of (a) an axial cross section of the blue/green zone and (b) a radial cross section of the grey/silver zone, where A, B and C highlight $LnBSiO_5$, $LiNaZrSi_6O_{15}$ and palladium (ruthenium) telluride phases, respectively; D indicates a fracture in the glass matrix*

checked by weighing the capsule prior to and after welding. The capsule was placed in a vertical cold-seal pressure vessel, as described by Dalton & Gibb[4] with water as a pressure medium. The capsule was mounted such that the long axis of the specimen was parallel to that of the pressure vessel. The bore of the pressure vessel was packed with steel rods to minimise convection and thermal gradients. The assembly was heated to 760°C (±1°C) at a pressure of 0·15 GPa over 12 h. Following reaction for 936 h, the vessel was quenched isobarically and the capsule recovered. The capsule was cleaned and dried to check for any mass loss during the experiment. The recovered specimen was examined by powder x-ray diffraction and scanning electron microscopy coupled with energy dispersive x-ray (EDX) spectroscopy.

Results and discussion

Examination of the simulant Magnox waste glass by electron microscopy and x-ray diffraction revealed the presence of needle-like RuO_2 crystallites, a few μm in size, and larger (5–20 μm) inclusions of a palladium telluride phase as shown in Figure 1(a). The observation of RuO_2 crystallites is not unexpected, given the low solubility of this material in alkali borosilicate glass.[5]

Following heat treatment at 760°C and 0·15 GPa for 936 h, the initially black core specimen of Magnox waste glass was found to be composed of two approximately equal parts: the upper part of the specimen (with respect to the orientation of the specimen in the furnace) was composed of a translucent blue/green glassy material whereas the lower fraction comprised a grey/silver opaque material, Figure 1(b). Powder x-ray diffraction revealed the lower grey/silver zone of the heat treated specimen to be composed of an amorphous phase and at least three crystalline phases; a stillwellite lanthanide borosilicate, $LnBSiO_5$ (Ln=Y, La, Pr, Ce, Nd, Sm and Gd); zektzerite, $LiNaZrSi_6O_{15}$; and at least one unidentified phase (possibly palladium telluride). In contrast, the diffraction pattern of the upper blue/ green zone of the heat treated specimen revealed this material to be essentially amorphous in nature, although a small amount of $LnBSiO_5$ was observed.

Optical and electron microscopy of the axial cross-section, confirmed the lower grey/silver zone to be composed of a fractured glass matrix and various crystalline phases, see Figure 1(b). No significant difference in the composition of the glass matrix in the upper and lower zones of the heat treated specimen was apparent from semi-quantitative EDX analysis. As shown in Figure 2(a), small hexagonal crystallites, ~5 μm in size, were observed on the surface of the blue/ green zone, to a depth of *ca*. 150 μm. These crystallites were identified from EDX/XRD as stillwellite, $LnBSiO_5$. Similar $LnBSiO_5$ crystallites were observed at the surface of the silver/grey zone, to a depth of 150–1000 μm as shown in the radial cross-section of the specimen, Figure 2(b). The inner boundary of this zone of crystallisation was defined by larger crystallites of $LnBSiO_5$ and $LiNaZrSi_6O_{15}$ which were 10–25

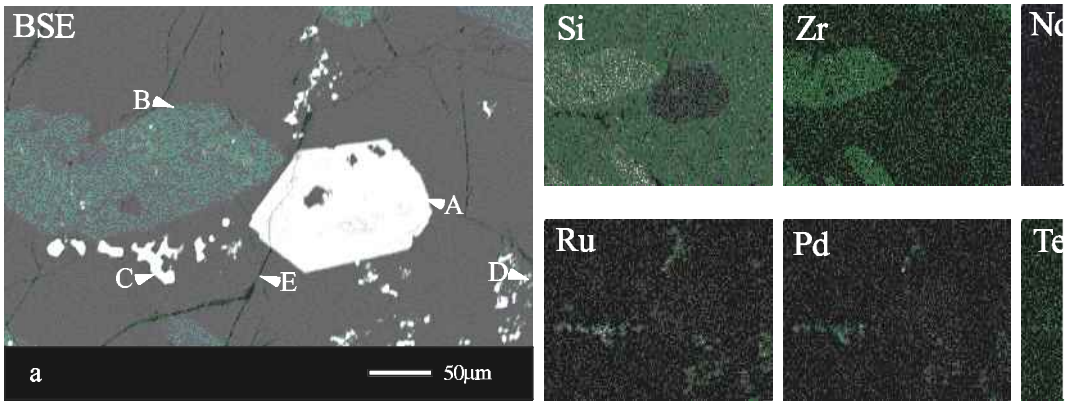

Figure 3. *Back scattered electron image and x-ray scanning images of a region from the radial cross section of the grey/silver zone; A, B, C and D denote $LnBSiO_5$, $LiNaZrSi_6O_{15}$, palladium (ruthenium) telluride and RuO_2 phases respectively; E indicates a fracture in the glass matrix*

μm in size. Large acicular crystallites of $LiNaZrSi_6O_{15}$, up to 150 μm in diameter and 1500 μm in length, and hexagonal crystallites of $LnBSiO_5$, 50–150 μm in size, were found within the interior of the grey/silver zone, as shown in Figures 1(b) and 2(b). Crystallites of $LiNaZrSi_6O_{15}$ and $LnBSiO_5$ and irregular 'droplets' of a palladium ruthenium telluride phase were also observed in the inner region of the silver/grey zone, as shown Figure 3. Small crystallites of RuO_2 were also apparent, Figure 3, although at a much lower volume fraction with respect to the starting material, Figure 1.

Conclusions

Heat treatment of Magnox waste glass at 760°C and 0·15 GPa for 936 h, clearly results in melting and partial crystallisation of this waste glass. Under these conditions, the glass is sufficiently fluid for more dense crystals to settle to the lower part of the specimen, where further crystal growth may occur. The difference in thermal expansion coefficient between the various crystalline phases and the glass matrix results in fracturing of the lower grey/silver partially crystallised fraction, on rapid cooling. Crystallisation of $LnBSiO_5$ is observed over the surface of the entire specimen. Interestingly, surface crystallisation of $LnBSiO_5$ is known to occur in glasses of the Ln_2O_3–B_2O_3–SiO_2 system.[6] In addition, some redistribution of Ru arises during heat treatment, with this element being partially accommodated in the palladium telluride phase. The irregular morphology of this phase suggests that it is fluid under the conditions of the experiment.

The partial crystallisation of Magnox waste glass under conditions of high temperature, very deep, geological disposal does not present any fundamental impediment to the disposal of high level nuclear waste glasses *via* this scheme, provided that the surrounding recrystallised granitic rock remains impervious to the infiltration of hydrous fluids, as is anticipated.[1,2] Recent results confirm that under the anticipated conditions of high temperature, very deep, geological disposal, complete recrystallisation of granite will occur, with any cracks and fissures being sealed by recrystallised microgranite.[4,7]

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