

## Vapour Phase Hydration of Blended Oxide – Magnox Waste Glasses

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### ABSTRACT

Vapour phase hydration studies of a blended Oxide / Magnox simulant high level waste glass were undertaken at 200°C, over a period of 5 – 25 days. The alteration of this simulant waste glass is characterised by a short incubation time of less than 5 days, leading to the formation of an alteration layer several microns thick. Following the incubation period, the alteration proceeds at a constant rate of  $0.15(1)\mu\text{m d}^{-1}$ . The distribution of key glass matrix (Si, Na) and waste (Cs, Zr, Nd, Mo) elements was found to vary significantly across the alteration layer. Vapour phase hydration leads to formation of surface alteration products, identified as smectite, zirconium silicate and alkaline-earth molybdate phases.

### INTRODUCTION

In the UK, high level waste (HLW) arising from the reprocessing of spent Oxide ( $\text{UO}_2$ ) and Magnox nuclear fuels is blended and vitrified in a lithium sodium borosilicate glass matrix [1]. The vitrified product is comprised of 25 wt% waste, on an oxides basis, derived from Oxide and Magnox HLW blended in a 75:25 ratio (by weight, on an oxides basis). At present, the vitrified waste, contained in carbon steel containers, is stored in air cooled silos awaiting a decision on final disposal. During interim storage, the initial surface temperature of the waste glass may be as high as 200°C, as a consequence of radiogenic heating. In the event of water becoming trapped in the ullage of the waste glass container (either during production or through a container breach which, subsequently, becomes sealed), vapour phase hydration may be an important mechanism of glass corrosion. Although this scenario is highly unlikely it should, nevertheless, be considered. The vapour phase hydration test also provides a means to compare the relative durability of nuclear waste glasses and is included in the performance criteria applied to the Low Activity Waste (LAW) glasses developed for remediation of the Hanford site [2]. The interaction between HLW glasses and water vapour may also be important in a humid repository environment [3].

The Vapour phase Hydration Test (VHT), recently standardised by Jiricka *et al* [4], provides a method for investigating the interaction between (simulant) nuclear waste glasses and water vapour. Essentially, the VHT methodology involves subjecting a glass specimen to vapour phase hydration in a sealed vessel at elevated temperature. Sufficient water is present in the vessel to allow a thin film of water to condense on the specimen at the reaction temperature,

leading to glass hydration, ion-exchange and network dissolution [5, 6]. As a consequence of these corrosion processes, the thin film of water becomes rapidly saturated in leached species which, at solubility limited concentrations, precipitate as “secondary” alteration products [5, 6]. The vapour phase hydration test therefore allows alteration products to be obtained in a short period of time.

Here, we report preliminary results from an investigation of the vapour phase hydration of a blended Oxide / Magnox simulant waste glass (referred to as OM7525 waste glass, with the composition given in Table I), compared with the behaviour of the French SON68 simulant HLW glass under nominally identical conditions [7, 8]. With respect to the SON68 waste glass, the OM7525 composition contains a higher level of  $\text{Li}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{B}_2\text{O}_3$  and  $\text{Gd}_2\text{O}_3$  but contains less  $\text{CaO}$ ,  $\text{ZnO}$  and transition metal oxides. The vapour phase hydration of OM7525 waste glass specimens, was studied at  $200^\circ\text{C}$  for periods of 5 – 25 days in saturated water vapour. The progress of alteration was monitored by measurement of the hydration layer thickness by Scanning Electron Microscopy (SEM). Analysis of the hydration layer and surface alteration products was performed using SEM coupled with Energy Dispersive X-ray spectroscopy (EDX) and X-ray diffraction.

**Table I.** Composition of the full scale OM7525 simulant waste glass employed in this study.

Component	Wt%	Component	Wt%	Component	Wt%	Component	Wt%
$\text{SiO}_2$	46.28	$\text{MoO}_3$	2.21	$\text{La}_2\text{O}_3$	0.87	$\text{Cr}_2\text{O}_3$	0.23
$\text{B}_2\text{O}_3$	15.9	$\text{CeO}_2$	1.86	$\text{Pr}_6\text{O}_{11}$	0.85	$\text{NiO}$	0.21
$\text{Na}_2\text{O}$	8.59	$\text{Cs}_2\text{O}$	1.60	$\text{SrO}$	0.55	$\text{K}_2\text{O}$	0.15
$\text{Li}_2\text{O}$	3.92	$\text{Al}_2\text{O}_3$	1.59	$\text{Sm}_2\text{O}_3$	0.44	$\text{P}_2\text{O}_5$	0.11
$\text{Gd}_2\text{O}_3$	2.92	$\text{MgO}$	1.41	$\text{Y}_2\text{O}_3$	0.36	$\text{TiO}_2$	0.06
$\text{ZrO}_2$	2.78	$\text{Fe}_2\text{O}_3$	1.10	$\text{TeO}_2$	0.31	$\text{HfO}_2$	0.06
$\text{Nd}_2\text{O}_3$	2.77	$\text{RuO}_2$	1.03	$\text{BaO}$	0.24	$\text{CaO}$	0.03

## EXPERIMENTAL

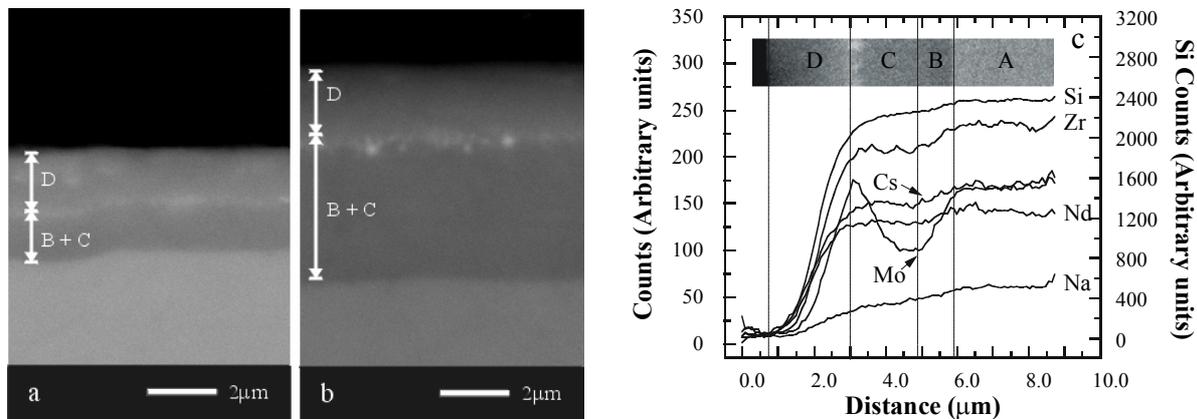
A sample of OM7525 simulant waste glass (~300g), produced during non-active commissioning of the BNFL waste vitrification plant, was broken down to a coarse ( $\leq 4\text{mm}$ ) cullet and melted in a platinum crucible at  $1060^\circ\text{C}$  in air. The cullet was allowed to melt over a period of one hour and then stirred for a further hour using a platinum paddle. The glass melt was cast into several bars of approximate dimensions  $15 \times 15 \times 100\text{mm}$ , annealed at  $500^\circ\text{C}$  for one hour and cooled, at a rate of  $1^\circ\text{Cmin}^{-1}$ , to room temperature. Parallel sided rods, of cross section  $10 \times 10\text{mm}$  were cut from the bars using a diamond saw, and sectioned to give coupons of dimensions  $10 \times 10 \times 1.5\text{mm}$  ( $\pm 0.25\text{mm}$ ). These coupons were polished using SiC paper, with water as a lubricant, to a finish of 800 grit, on all sides. The polished coupons were cleaned ultrasonically in isopropanol and dried at  $110^\circ\text{C}$ .

VHT experiments were performed in Parr series 4700 pressure vessels (fabricated from Type 316 stainless steel) with a volume of  $22\text{cm}^3$ , according to the procedure described by Jiricka *et al* [4]. Two coupons were suspended in the centre of each pressure vessel using support frames and thin wires of Type 304 stainless steel. Sufficient deionised water, 0.2ml, was added to each pressure vessel to saturate the volume of the vessel at the reaction temperature of

200°C and provide for a non-dripping layer on the surface of the coupons. The pressure vessels were sealed, with the aid of a Teflon™ gasket, and placed in a convection oven at 200°C ( $\pm 1^\circ\text{C}$ ) for 5 – 25 days. At the end of each test, the vessels were removed from the oven and quenched in a shallow bath of cold water. On opening the vessels, the coupons were removed and the pH of the condensed water measured using universal indicator paper, to ascertain whether dripping of water from the coupon had occurred during the test (confirmed by a  $\text{pH} > 7$ ). No evidence for vessel leakage or dripping of water from the coupons was apparent in any of the tests. Coupons for analysis by SEM were mounted on aluminium stubs (using silver paint) or in cold-setting epoxy resin and polished to a 1  $\mu\text{m}$  finish with an oil based lubricant. All specimens were carbon coated and analysed using a JEOL JSM-5600 SEM coupled with a PGT EDX system or a JEOL JSM-6400 SEM with an Oxford Link EDX system. X-ray diffraction data were acquired using a Philips 1410 diffractometer with Co-K $\alpha$  radiation, operating in reflection mode with a diffracted beam monochromator

## RESULTS AND DISCUSSION

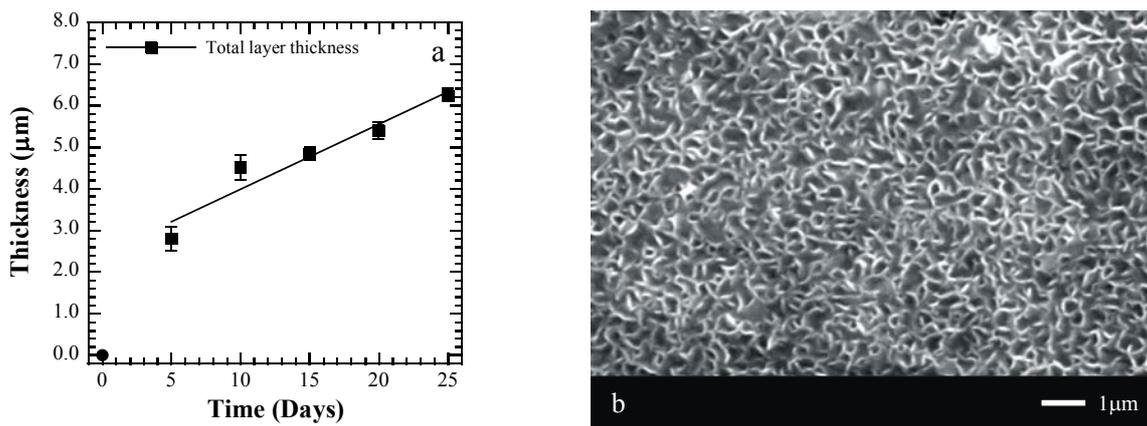
A thin, uniform, alteration layer, several microns thick, was observed in the back-scattered electron images of the cross sections obtained from coupons treated for 5 - 25 days at 200 °C, as shown in Figure 1.



**Figure 1.** Back-scattered electron image of the cross section obtained from a coupon subject to vapour phase hydration conditions at 200 °C for a) 5 days and b) 25 days; profile of selected elements across the alteration layer of a coupon subject to vapour phase hydration for 15 days at 200°C (note: left hand scale refers to all elements except Si).

The alteration layer was observed to be comprised of two distinct parts (Zones D and B + C) separated by a thin band of bright contrast that is composed of distinct bright spots, as shown in Figure 1. EDX line scans were performed on the alteration layers to determine the distribution of key waste (Zr, Cs, Mo, Nd) and glass matrix (Si, Na) species within these layers. Zone B, corresponding to the inner band of darker contrast in back-scattered electron images, is characterised by a concentration gradient in all elements. Zone C is characterised by a shallow

concentration gradient in Na and Si, whereas the concentration of Zr, Cs and Nd is essentially invariant. The Mo concentration is depleted in the lower half of Zone C but increases rapidly in the upper half of this zone, at the interface with Zone D, corresponding to the thin band of bright contrast in back scattered electron images. A steep concentration gradient in all elements is observed in Zone D. The total thickness of the alteration layer was found to increase with reaction time, see Figure 2a. The rate of alteration, determined from a non-linear least-squares regression to the total thickness data, was  $0.15(1)\mu\text{m}\text{d}^{-1}$ .

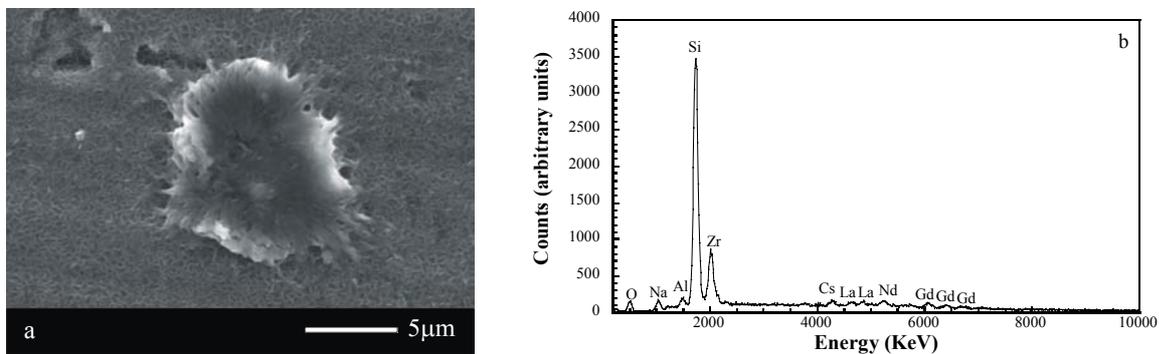


**Figure 2.** a) Evolution of alteration layer thickness as a function of time (error bars denote  $3\sigma$ ) and b) Secondary electron image of the sodium aluminosilicate layer present on the surface of a 25 day coupon.

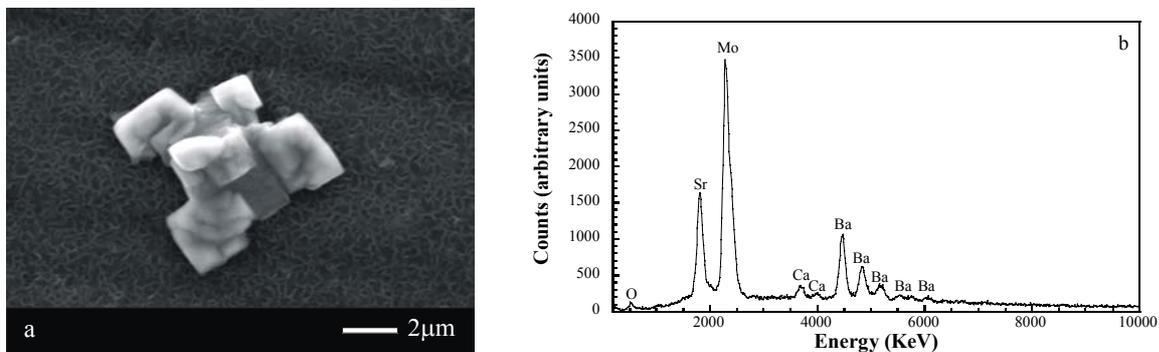
Secondary electron images of the surfaces of specimens treated for 5 – 25 days at  $200^\circ\text{C}$  revealed the formation of an extensive aluminosilicate layer with a honeycomb-like microstructure, as shown in Figure 2b. This phase was identified by X-ray diffraction as a smectite-type clay, Nontronite, with a basal (001) spacing of  $14.6\text{\AA}$  (with the possible general formula  $(\text{Na},\text{M})_x(\text{Si},\text{Al},\text{A},\text{M})_4\text{O}_{10}(\text{OH})_2\cdot 4\text{H}_2\text{O}$ , where M and A denote, respectively, a transition metal and lanthanide or calcium cations). The honeycomb-like microstructure of this material is similar to that of the smectite layer observed on the surface of SON68 waste glass specimens treated under nominally identical conditions [7, 8]. This layer is not observed on the surfaces of the cross sectional specimens examined by SEM (Figures 1a and 1b) indicating that the thickness of this layer is below the resolution of the instrument,  $\sim 0.1\mu\text{m}$ . This is consistent with the thickness of the smectite layer observed on altered SON68 specimens which was found to be  $< 0.1\mu\text{m}$  thick from TEM studies [7]. In addition to the smectite layer, irregular zirconium silicate and cuboidal alkaline-earth molybdate alteration products were observed on the surface of all specimens, as shown in Figures 3 and 4, respectively. The alkaline-earth molybdate phase, which was also found to occur as irregular flat platelets, several microns in size, was tentatively identified as a powellite related mineral,  $(\text{Ca},\text{Sr},\text{Ba})\text{MoO}_4$ , by X-ray diffraction. The surface coverage and mean size of these alteration products was observed to increase with reaction time.

Vapour phase hydration of simulant nuclear waste glasses is generally characterised by an incubation period followed by a rapid increase in the rate of alteration which, subsequently, decreases and proceeds at a slower, constant, rate [3, 4, 9]. The rapid increase in alteration rate

is associated with the precipitation of alteration products and the subsequent period of slow alteration may be interrupted by additional rapid rate excursions as further alteration products are formed. Figure 1b demonstrates that vapour phase hydration of OM7525 waste glass follows the general pattern of alteration, with a constant rate of alteration achieved in less than 5 days. The thickness of the alteration layer observed on OM7525 waste glass after 20 days,  $\sim 5\mu\text{m}$ , is significantly greater than that observed on the French SON68 waste glass,  $\sim 0.05\mu\text{m}$ , after 21 days under nominally identical conditions [7]. The somewhat lower durability of OM7525 waste glass is most likely due to the higher  $\text{Li}_2\text{O}$  and  $\text{B}_2\text{O}_3$  content of this glass, with respect to the SON68 composition. Vapour phase hydration studies of Low Activity Waste glasses for remediation of the Hanford site have also demonstrated that Li has a deleterious effect on glass durability [4].



**Figure 3.** a) Secondary electron image and b) EDX spectrum of the zirconium silicate alteration phase on the surface of a coupon subject to VHT conditions at 200°C for 25 days.



**Figure 4.** a) Secondary electron image and b) EDX spectrum of the alkaline earth molybdate alteration phase on the surface of a coupon subject to VHT conditions at 200°C for 25 days.

Vapour phase hydration of OM7525 waste glass appears to proceed *via* the penetration of a hydration front into the pristine glass at a rate of  $0.15(1)\mu\text{m d}^{-1}$ , leaving behind a diffusion layer (Zone B) in which the glass matrix (Si, Zr) and modifier (Na, Cs, Mo and lanthanides) elements are depleted. The inner part of the gel layer (Zone C) is characterised by a redistribution of Mo, a slight depletion of Na and Si whereas the concentration of Cs, Zr and Nd remains essentially constant; all elements are depleted in the outer part (Zone D) of the gel layer. The leached

species are immobilised in the smectite, zirconium silicate and alkaline-earth molybdate surface alteration products.

## CONCLUSIONS

The vapour phase hydration of OM7525 waste glass results in the formation of an alteration layer several microns in thickness and smectite, zirconium silicate and alkaline-earth molybdate alteration products. After 5 days of reaction at 200°C in saturated water vapour, the alteration proceeds at a constant rate of  $0.15(1)\mu\text{m d}^{-1}$ . The thickness of the alteration layer observed on OM7525 waste glass after 20 days is approximately an order of magnitude greater than that observed on the French SON68 waste glass after 21 days, under nominally identical conditions. This may be attributable to the higher  $\text{Li}_2\text{O}$  and  $\text{B}_2\text{O}_3$  content of OM7525 waste glass with respect to the SON68 composition. The data reported here will be combined with experimental data relating to the cooling and fracture of full scale waste glass products and suitable modelling codes to predict the possible effect of water vapour corrosion on the full scale glass wasteform during interim storage.

## ACKNOWLEDGEMENTS

We gratefully acknowledge the assistance of Dr. J.W. Roberts, Mr. I.P. Watts and Mr. P. Staton (The University of Sheffield) and Mr. E. Graham (BNFL) in undertaking this study. This work was funded in part by BNFL Plc.

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