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Interactions between Simulant Vitrified Nuclear Wastes and high pH solutions: A Natural Analogue Approach

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ABSTRACT

This study details the characterisation of glass samples exposed to hyperalkaline water and calcium-rich sediment for an extended time period (estimated as 2 - 60 years) at a lime (CaO) waste site in the UK. We introduce this site, known as Peak Dale, in reference to its use as a natural analogue for nuclear waste glass dissolution in the high pH environment of a cementitious engineered barrier of a geological disposal facility. In particular, a preliminary assessment of alteration layer chemistry and morphology is described and the initiation of a long-term durability assessment is outlined.

INTRODUCTION

Owing to a long history of encapsulation of radioactive wastes in cementitious materials, the proposed geological disposal facility (GDF) of the UK will most likely incorporate a significant volume of cement. In addition to 450,000 m^3 of cement-encapsulated waste[1], the facility may also use a cementitious backfill as part of the engineered barrier, which will be optimised to physically and chemically impede the transport of radionuclides to the biosphere[2]. Over geological time scales, groundwater will interact with the cementitious components of the facility resulting in high pH conditions in the repository[3]. Should vitrified intermediate level waste be placed in this environment, an understanding of the effect of cement leachates on the longevity of glass is required.

We describe a new natural analogue site for long-term glass durability assessment in high pH, cement-like leachates, including a preliminary assessment of the physical and chemical conditions and their effects on glass samples recovered from the site.

METHODOLGY

Site and sample description

The Peak Dale Tunnel site is a disused railway tunnel, constructed in the early 20th century, to link the Peak Dale limestone quarry to its associated limekilns. The waste produced from the limekilns is distributed in a thick layer (1 – 2 m) of lime (CaO) over the soil and bedrock of the surrounding area [4]. This has seeped through to the tunnel below, creating a naturally hyperalkaline ground water and Ca-rich sediment. Access to the tunnel was restricted to the public when a locked gate barred the entrance. A number of glass bottles were found to be exposed to these high pH conditions for an estimated period of time between 2 and 70 years, four samples are being examined due to their varying compositions and large proportions of the bottle remains intact.

Site characterisation

The tunnel has a stable temperature ranging from 8 – 9 ± 0.5 °C [4]. A sample of sediment was taken from a depth of 1 - 4 cm and dried in air prior to sieving to a particle size of < 75 μm for X-ray diffraction (XRD) analysis. XRD data were acquired using a Bruker D2 Phaser, with Cu Kα radiation, from $5^{\circ} < 2\theta < 70^{\circ}$ with a step size of 0.01°. The X-ray tube settings were 30 kV and 10 mA.

The water level in the tunnel varies throughout the year, but the back of the tunnel is flooded permanently to a depth of 1-1.5 m^2. Alkaline ground water was sampled from standing water at two locations in the tunnel; the first is periodically subject to complete evaporation (referred to herein as the "beach"), and the second is a deep central pond. Samples were filtered (0.22 μm), acidified with nitric acid and analysed for major elemental content using inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis (Thermofisher, iCAP Duo).

Glass sampling, preparation and analysis

The glass samples found at the site were removed from beneath the sediment. In the laboratory, glass samples were air dried then sectioned using a diamond slow saw. Compositional analysis via acid digest and ICP will be determined for all glass samples found at the site, samples were prepared for Scanning Electron Microscopy (SEM) by mounting in epoxy resin and grinding the cross-sectional surface on silicon carbide paper (P600, 800 and 1200, respectively), followed by polishing using diamond suspension 6, 3 and 1 μm. The sample was carbon coated prior to inspection on the SEM. Imaging was performed using an FEI Quanta 200 F SEM with EDX using an accelerating voltage of 20 kV and a working distance of 10 mm.

RESULTS AND DISCUSSION

Figure 1 shows the location of the Peak dale site in the UK (Fig 1a), and the tunnel is shown in Fig. 1b. The stalactites and stalagmites demonstrate the propensity for lime waste leaching into the tunnel from above.

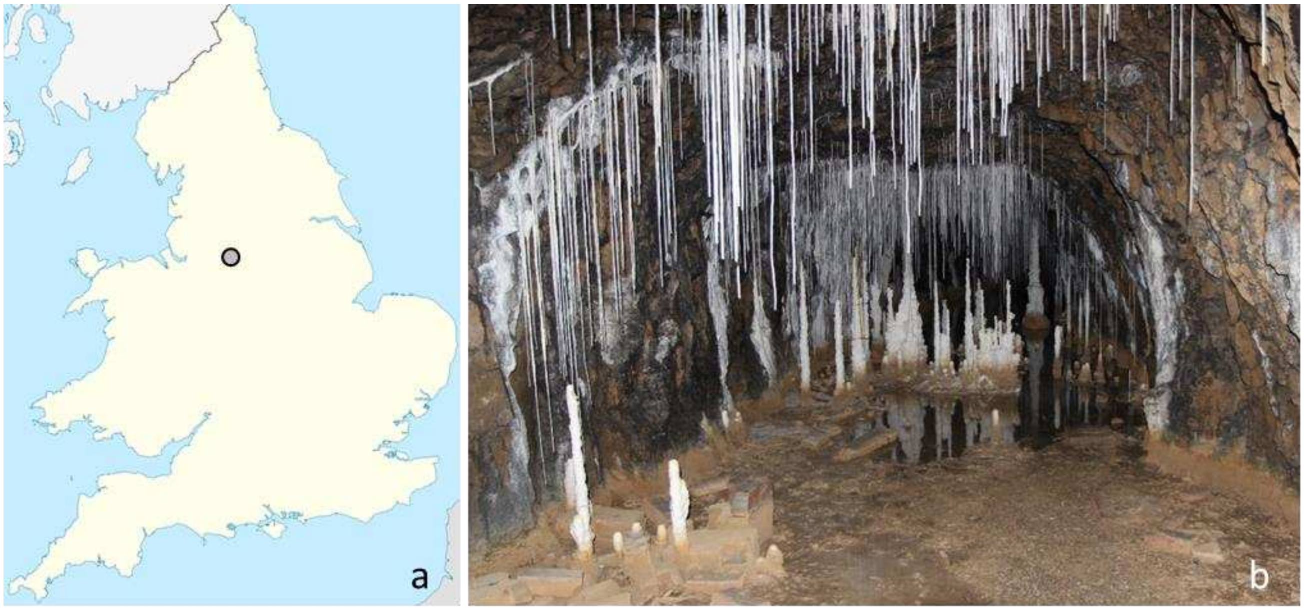

Figure 1 (a) Map of the UK with the location of the Peak Dale Tunnel; (b) photograph of the Peak Dale tunnel.

Analysis of the tunnel sediment by XRD (Figure 2) revealed a composition of calcite ($CaCO_3$), which is formed when the hydrated limewaste ($Ca(OH)_2$) is in equilibrium with atmospheric $CO_{2(g)}$. This is a major difference between this natural analogue site and a GDF, as there will be no atmospheric CO_2. However, low concentrations of $CO_{3(aq)}$ will be present in the GDF ground water[5], albeit at a much lower concentration than at the Peak Dale site.

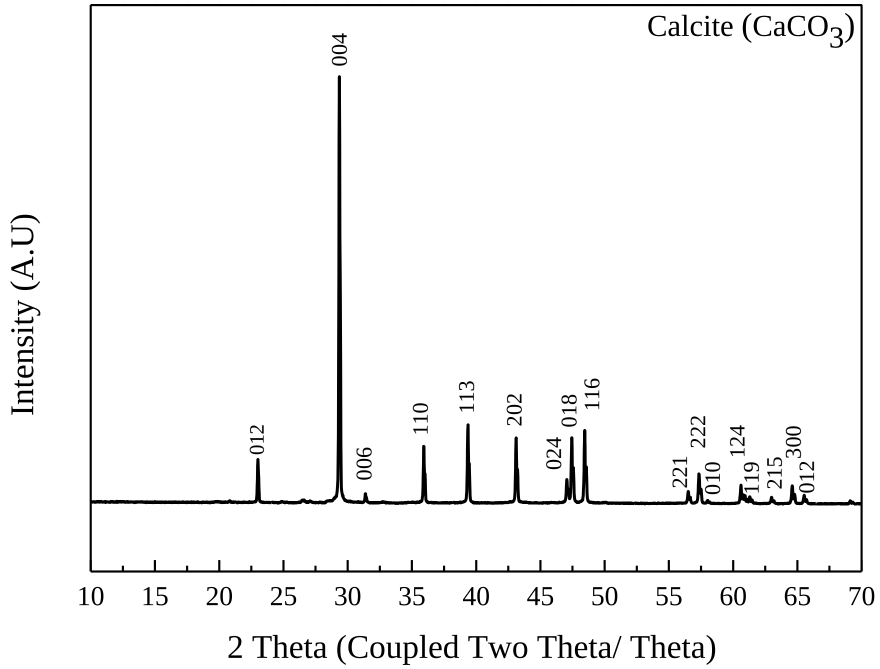

Figure 2. X-ray diffraction pattern of sediment from the central pond in the Peak Dale tunnel.

The pH of the water was measured as pH 12.79 ± 0.5. Table I. shows the analyzed concentration of major elements in the two sample locations within the tunnel. For comparison, the composition of three synthetic cement waters are shown. Hyperalkaline cement water will evolve, from an initial potassium rich leachate (pH~13) represented here by young cement water, to a Ca-OH fluid (pH 10 - 12.5) buffered by the dissolution of portlandite ($Ca(OH2)$). Subsequent dissolution of calcium silicate hydrate phases, represented here by the evolved cement water, will occur and finally an old cement water, with a similar composition to ground water will be present in the GDF [6,7]. The Na value from the central pond at Peak Dale is anomalously high when compared to the value from the beach, which is attributed to grit salt on the nearby roads. The water sample from the beach is comparable to the synthetic evolved cement water, given its low K concentrations and alkalinity being governed by Ca and Na hydroxides.

Table I. Elemental concentration (mg L^{-1}) of standing water from the Peak Dale site, compared with synthetic formulations of cementitious ground waters. Errors stated are based on the standard deviation across the range of measurements.

Element	**Peak Dale Central Pond**	**Peak Dale Beach**	Synthetic Young Cement Water + Ca	Synthetic Evolved Cement Water	Synthetic Old Cement Water
Al	**0.76 ± 0.02**	**0.06 ± 0.02**	-	0.09 ± 0.06	0.01 ± 0.04
Ca	**34.82 ± 0.09**	**332.50 ± 0.76**	15.24 ± 0.74	503.53 ± 3.48	33.58 ± 3.41
K	**22.61 ± 0.08**	**19.93 ± 0.03**	9415.67 ± 18.50	6.72 ± 0.29	0.44 ± 0.75
Na	**1027.31 ± 0.72**	**421.80 ± 0.47**	1595.33 ± 6.85	373.47 ± 10.90	105.67 ± 3.47
S	**35.23 ± 0.08**	**286.20 ± 0.47**	35.88 ± 0.49	0.14 ± 0.015	2.75 ± 0.32
Si	**8.53 ± 0.04**	**8.61 ± 0.05**	0.05 ± 0.02	0.19 ± 0.07	0.02 ± 0.01

The sediment layers and surface morphology of one of the glass samples recovered from the Peak Dale tunnel are shown in Figure 3. A thick (1.0 ± 0.1 mm) alteration layer was observed on the surface of the glass (Fig. 3a), which was banded; this is postulated to be due to repeated wetting and drying as the water level in the tunnel fluctuates throughout the year. The elemental map shown in Figure 3b indicates that these layers are rich in calcium, which is in good agreement with the presence of high quantities of calcite in the sediment (Fig. 2). It is therefore likely that the mineral phase present in the alteration layer is also calcite ($CaCO_3$).

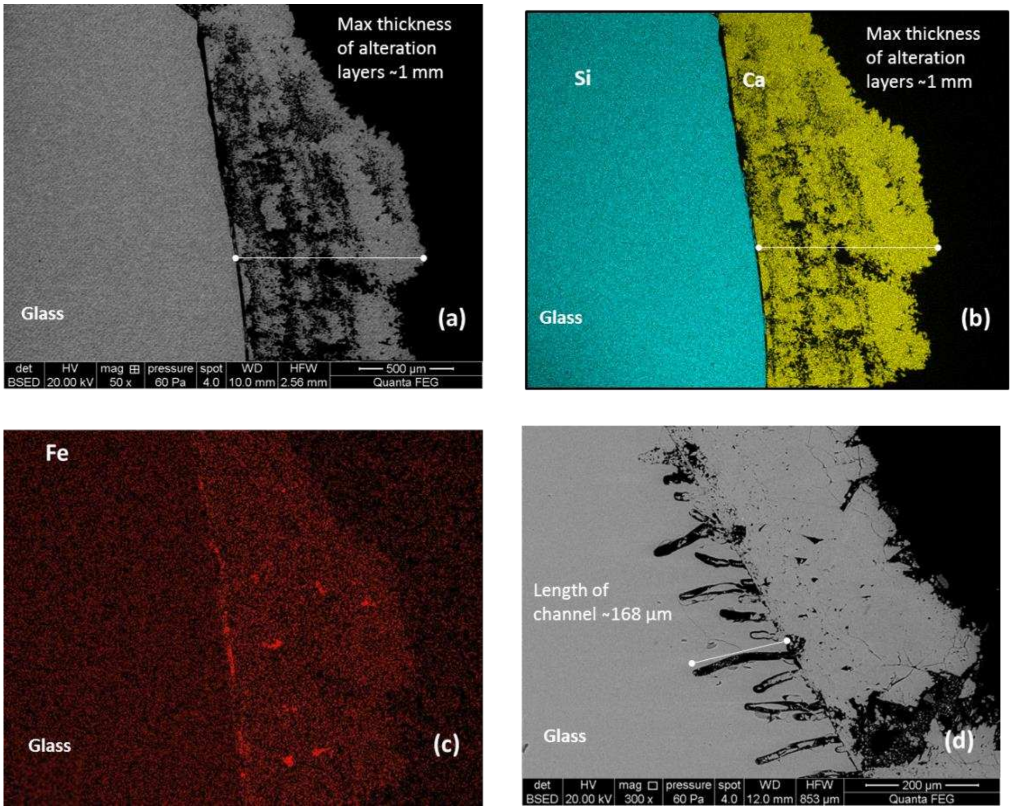

Figure 3. Scanning electron micrographs of a glass sample from the Peak Dale tunnel: **(a)** BSE image of the alteration layer; **(b)** elemental mapping showing distribution of Ca and Si and **(c)**, iron **(d)** BSE image, showing chemiturbation channels at the interface between the sediment on the surface and bulk of the glass.

The main source of iron in the Peak Dale tunnel is from the remnants of steel cables that are now severely corroded. This appears to have been sequestered at the interface between the glass and the alteration layer, as shown in Figure 3d. It is also observed in pores in the banded regions of the alteration layer. Canister corrosion will result in iron accumulating in a GDF; it has been shown that the presence of iron corrosion products can affect the initial stage of glass alteration. Silica can sorb to iron corrosion products, retarding the formation of a silica gel layer on the surface of the glass[8]. It is also been shown that silica precipitates on magnetite (Fe_3O_4) and Fe-silicates in the surroundings or within the porous gel layer if iron rich compounds are present[9]. The presence of iron in the tunnel allows investigation into how iron will affect the dissolution of simulant UK nuclear waste glasses.

Figure 3d shows chemiturbation channels < 200 μm in length. This inward corrosion originates from the surface of the glass and proceeds towards the bulk. The origin of these channels is not yet understood, however, potential causes may be: damage to the glass surface, exposing regions of tensile stress that corrode more rapidly than the surrounding areas; repeat wetting and drying resulting from seasonal changes in the water levels; and morphological features that are, in essence, high energy sites that promote dissolution. Further work is underway to determine the origin of these features.

Future use of the Peak Dale tunnel as a natural analogue for understanding long-term glass dissolution

The conditions at the Peak Dale site are suitable for conducting a long term natural analogue study; a hyperalkaline environment with ground water that is comparable in composition to an evolved cement leachate. In addition a steady all year round temperature and sufficient water levels will allow the submersion of glass samples for an extended time period of up to 10 years.

The following vitrified waste simulants will be placed within a bespoke sample holder (Figure 4a-c) and immersed within the tunnel water: the International Simple Glass (ISG); UK Magnox waste glass (MW); vitrified UK plutonium contaminated material (PCM); prototype vitrified ion exchange resin waste; a laboratory waste simulant (LBS); SON68 and a re-melted composition of one of the glass bottles originally found in the tunnel.

Samples will be removed at 1, 3, 5 and 10 years, and alteration layers will be characterised by SEM/EDX, glancing incidence XRD, time of flight secondary ion mass spectrometry (TOF-SIMS) and transmission electron microscopy (TEM). This will develop our current knowledge of the chemical composition of alteration layers within this hyperalkaline environment and aid our understanding of the long-term durability of nuclear waste glass.

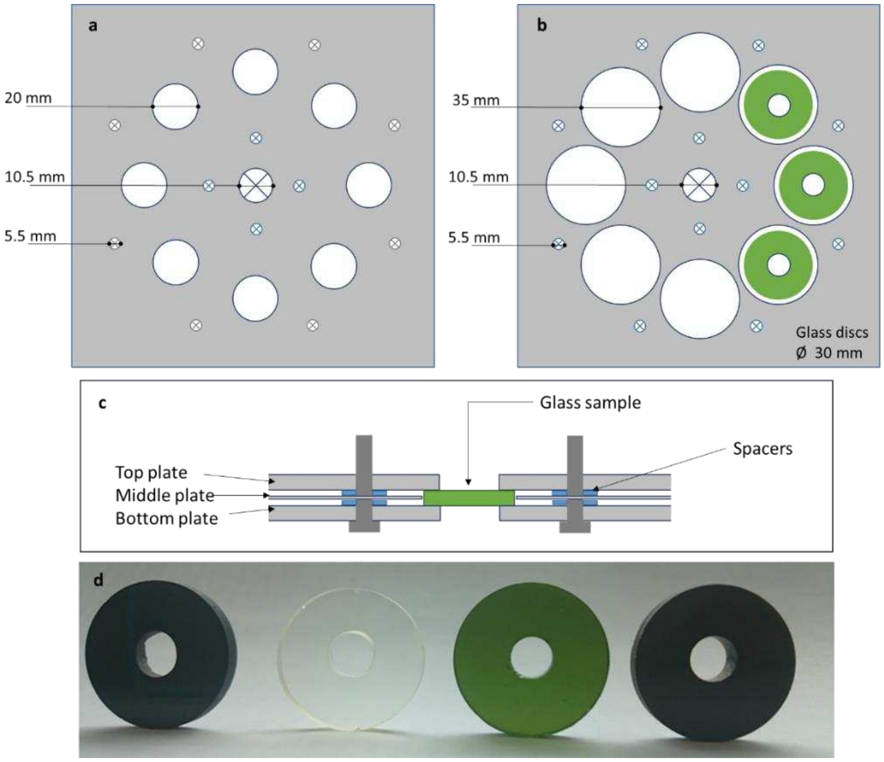

Figure 4. Schematic of sample holder **(a)** top and bottom plate 5mm thick PTFE used to sandwich glass samples **(b)** middle plate 1mm thick PTFE, holds glass samples in position **(c)** side view of the sample holder **(d)** glass samples left to right PCM, ISG, MW, LBS.

CONCLUSION

The Peak Dale site has provided glass samples with significant alteration layers due to an extended exposure in hyperalkaline ground water and Ca-rich sediment, the composition of which is similar to evolved cement water that will occur within a GDF over geological time scales. The presence of chemiturbation channels at the surface of the glass sample require further research in order to understand how they develop, and to quantify their effect on the long term durability of glass wasteforms. The site is suitable for a long term durability study investigating simulant nuclear waste glasses relevant to the UK disposal scenario in the natural environment despite the presence of air and a temperature of ~ 9 ^{o}C. The results generated from this study will provide information on the long-term behaviour of vitrified waste materials within a cementitous geological disposal facility.

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