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Real time, in-situ deuteriding of uranium encapsulated in grout; effects of temperature on the uranium-deuterium reaction

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ABSTRACT

To accurately predict the initiation and evolution of uranium hydride potentially present in nuclear waste containers, studies of simulated conditions are required. Here, for the first time, the uranium-deuterium reaction was examined in-situ, in real time, whilst within grouted media. A deuterium gas control rig and stainless steel-quartz glass reaction cell were configured on a synchrotron beam line to collect X-ray diffraction and X-ray tomography data. It was found that deuteride formation was limited by the uranium and grout thermal conductivities and deuteride initiation only commenced above a threshold temperature. Strong adherence between uranium oxide and grout was also observed.

1. Introduction

In the UK, challenges have arisen regarding the safe packaging and storage of Intermediate Level nuclear Waste (ILW), which has now been classified as highly active waste due to the processing of Magnox uranium metal fuel. The ILW consists of de-canned Magnox swarf and irradiated uranium metal which have been encapsulated in a grout, sealed in 500 L stainless steel containers and subsequently left in storage where corrosion has progressed in a moist, highly alkaline, environment [1].



Chemical transformation of the uranium metal (19.1 g cm⁻³ [2]) to uranium oxide (10.9 g cm⁻³ [3]) (Eq. (1)), and potentially uranium hydride (UH₃) (10.95 g cm⁻³ [4]) directly (Eq. (2)), or indirectly (Eqs. (3)–(4)) [5–7] causes an almost doubling in material volume, which then exerts considerable physical pressure on the surrounding grout and steel. If volume expansion is extreme, this poses a risk of containment failure during storage or transportation [7,8]. Production of uranium hydride is particularly hazardous since the corrosion product typically forms as a fine powder that has shown pyrophoric properties [9,10].

Thus, an influx of air as a consequence of containment failure could be highly undesirable. It is, therefore, important to understand and predict the extent of corrosion of uranium metal within these containers, with special attention given to hydride formation and distribution.

A number of variables affect the uranium-hydrogen reaction; among these, the effect of temperature on the rate of uranium hydride formation is well documented [11–14]. Reportedly, the reaction rate increases with increasing temperature (up to ~280 °C), when the competing reverse reaction (de-hydrating) begins [15]. However, it is unclear whether the hydrating reaction is dependent on the temperature of the metal, gas or both. In current storage areas, and potentially in a Geological Disposal Facility (GDF), ILW containers are stacked in close proximity to one another. The curing of grout in the containers (and surrounding the containers in a GDF) over many years is expected to cause an increase in ambient temperature, of up to 80 °C [16]. Warm post-reactor metals (Magnox alloy, uranium, aluminium) and curing grout have varying thermal conductivities (uranium = 22.5 W m⁻¹ K⁻¹ [17], grout 30+ % BFS = < 1.05 W m⁻¹ K⁻¹ [18]) and this will have an effect on dissipation of heat, potentially allowing conditions for instigation of uranium-hydride formation (if sufficient H₂ is present). To examine this behaviour, in-situ experiments investigating uranium corrosion when encapsulated in grout are required.

The importance of performing in-situ laboratory experiments for the study of metal corrosion is becoming increasingly apparent [19]. To accurately examine the mechanisms and rates of reactions, such as

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metal hydriding, it is vital to keep the sample conditions controlled and constant throughout the chemical reaction and during transfer into analytical instrumentation. This is typically problematic due to the physical configurations of common analytical instruments, which often require sample re-mounting or change of containment to allow the experiment to proceed. However, the following experiment presents an example of how in-situ study can be achieved: a custom made stainless steel-quartz glass reaction cell containing grout-encapsulated uranium metal was used to examine the uranium-deuterium reaction live, on the I12 (Joint Engineering, Environment and Processing) beam line at the Diamond Light Source (DLS). As this was designed as a feasibility study, a full evaluation of this method will be described throughout this paper.

2. Materials and methods

2.1. Sample preparation

An unirradiated Magnox uranium metal disc (0.7062–0.7158 wt% ^{235}U , 24 mm diameter and 2 mm thick), sourced from Springfields Ltd, was coarsely abraded sequentially using SiC grit paper from grades p300 to p2500 on all surfaces, and water as lubricant. The composition of the uranium disc is displayed in Table 1. A 0.5 mm \times 0.5 mm \times 20 mm section was cut from the metal disc using a Struers Accutom and the resulting uranium rod was again abraded using p2500 SiC grit paper to remove residual swarf. The sample was then allowed to oxidise in air for 2 h to ensure the entire surface had reached a similar oxide thickness and, thus, all ongoing corrosion reactions occurred via this pre-existing interface. The oxidised uranium rod was then cylindrically cast in a grout consisting of coarsely ground Blast Furnace Slag (BFS) and Ordinary Portland Cement (OPC) in a 3:1 ratio and 0.4 w/c (de-ionised water). The BFS (Redcar steel works) and OPC (Castle Cements) complied with the specification for materials used for ILW encapsulation by Sellafield Ltd, typical compositions are shown in Utton et al. [20]. The grouted sample (13 mm diameter and 35 mm in length) was cured in a moist environment for 3 days before transfer to normal humidity for 2 weeks.

To compare the deuteriding behaviour and highlight the in-situ capability of this set-up, a second sample was made using exactly the same method as above, except that the uranium rod was not encapsulated in grout and the metal was stored in air for 2 weeks prior to examination.

2.2. In-situ capability

The grout-encapsulated sample was transferred into a custom-made, quartz glass-stainless steel (316), reaction cell for transfer to DLS and experimentation. This cell was gas-tight (held a vacuum in excess of 1×10^{-6} mbar) and heat compatible to 300 °C. Fig. 1 displays details of the key components of the cell. To reduce the induction period of the uranium- D_2 reaction, the grout-encapsulated sample was first dewatered by heating overnight at 80 °C under a vacuum of 1×10^{-5} mbar in a clamshell furnace. The sample was sealed under vacuum and transported to DLS.

Table 1

The composition detected from the uranium metal disc using energy dispersive x-ray analysis. Beam energy and current of 10 keV and 2.8 nA, respectively, were used.

Element	Weight%
Si	0.06 \pm 0.04
Al	0.20 \pm 0.06
O	1.73 \pm 0.87
N	1.94 \pm 0.20
C	12.37 \pm 0.81
U	88.15 \pm 1.32

On the I12 beam line, a 316 stainless steel gas control rig was constructed (8.09×10^{-5} m³ reaction volume), including a Pfeiffer HiCube 80 Eco turbo pumping station, a deuterium (D_2) LaNi₅ bed (Sigma Aldrich 99.96 atom% D_2), a large 316 stainless steel 10 L volume (emergency empty volume for D_2 gas pressure removal) and an absolute pressure transducer (0–1 bar \pm 0.01 mbar precision) connected by Swagelok 6.35 mm diameter (1/4 inch) 316 stainless steel tubing and controlled using bellow valves. To heat the sample, a filament heater made from a quartz glass sleeve and 8 ohm nichrome resistance wire was placed on top of the reaction cell (Fig. 2). This was manipulated by a temperature PID controller and a thermocouple built into the base of the cell (at location 6 via a t-joint in Fig. 1). Radiography was used to position the uranium metal half within the filament heater, with the remaining sample located above the heated section (Fig. 2). Reaction with D_2 was chosen rather than H_2 to permit future analysis via mass spectrometry. It has been previously reported that the uranium- H_2 and uranium- D_2 reactions do not show significant isotopic differences in reaction rate or characteristics [21], thus all results here are considered comparable to uranium- H_2 studies elsewhere or in ILW environments.

2.3. Reaction conditions

Once all equipment was leak tested and in place, the first grout-encapsulated sample was heated to 170 °C and left to stabilise for 1 h prior to D_2 exposure. A fixed volume of 750 mbar D_2 was then released into the sealed reaction cell. After an induction period of 24 min, a pressure drop was measured as a direct result of the uranium- D_2 reaction. The reaction was ceased by evacuating all gas from the reaction cell after a 61 mbar pressure reduction was recorded (equating to 127 μmol D_2 reacting with the uranium metal).

The second bare sample was reacted using the exact same method. However, the reaction was performed at 120 °C, 650 mbar D_2 and was periodically stopped after 6, 9, 39 and 126 mbar D_2 uptake (equating to a total of 15, 22, 97 and 312 μmol D_2 reacting with the uranium metal) by removing the reactant gas, then keeping the metal under vacuum and restarting the reaction by adding fresh D_2 . This method allowed examination of the progressively D_2 reacted uranium metal.

2.4. Synchrotron parameters

During the pressure drop of the first encapsulated sample, in-situ X-ray powder diffraction (XRPD) measurements were recorded every 10 s over a 340 μm \times 340 μm area at the top of the sample. Immediately after the sample was reacted with D_2 , XRPD line scans, radiography images and tomography scans (XRT) (1.3 μm \times 1.3 μm per pixel) were taken along the vertical length of the sample. Limitations of these techniques with respect to examining uranium in grouted environments have already been discussed in [7,8].

At the time of examination, DLS was operating at a reduced beam current of 136 mA which resulted in a lower photon flux and, thus, lower contrast in the XRT scans and a generally reduced signal. An energy of 115.2 keV was used for both XRT and XRPD. 2D XRPD data were recorded using a flat panel Pixium RF4343 (Thales) in high resolution mode (2880 pixels \times 2881 pixels). This detector has a pixel size of 148 μm \times 148 μm and beam footprint of \sim 340 μm \times 340 μm on the sample surface. A CeO_2 standard (NIST – Standard Reference Material 674b) was used to calibrate the beam. A high speed Vision Research Phantom v7.3 imaging detector with the Module 4 camera (field-of-view 3.3 mm \times 2.8 mm) was used for imaging radiography and XRT with the monochromatic beam. Avizo[®] was used for the production of 3D tomographic visualisations.

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