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The behavior of advanced gas reactor simulated spent nuclear fuels in wet interim storage conditions

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The safe interim storage of spent nuclear fuel is important to prevent the degradation of the containers and fuel rods – both fuel pellets and cladding – thus avoiding the release of radiation and allowing the fuel to be safely handled on transfer to a long term disposal facility. The corrosion of pure UO_2 and UK Advanced Gas-cooled Reactor (AGR) simulated spent nuclear fuels (SIMFUELs) was studied under conditions typical of those found in interim spent fuel storage pond waters. With respect to the dissolution of spent fuel, it appears to be advantageous to dose the ponds to pH≈11.4. The alkaline conditions in the pond water suppress the dissolution as UO_2^{2+} which may otherwise occur at neutrality and lower pHs.

Keywords: corrosion; uranium; wet interim storage

1. Introduction

The bulk of the UK's operating fleet of nuclear reactors are of the Advanced Gas-cooled Reactor type (AGR). These were constructed during the 1970s and 1980s and utilize a graphite moderator and CO_2 gas coolant. AGR fuel consists of low enriched UO_2 annular ceramic pellets, encased in a 20/25/Nb stainless steel cladding. Currently, spent nuclear fuel (SNF) from these reactors undergoes reprocessing at the Thermal Oxide Reprocessing Plant (THORP) in Sellafield, Cumbria, where the spent fuel components are separated. Unused uranium and plutonium can be sent to form new fuel, and the fission products present in the fuel can be removed for disposal as high-level waste.

However, THORP is due to close within the next 2 years. The plan for current holdings of un-reprocessed AGR SNF and SNF that will be discharged from AGRs in the future is to send it to a national Geological Disposal Facility (GDF). The intention is for the GDF to start taking intermediate level waste (ILW) in the late 2030s, with fuel to follow after the disposal of the bulk of the accumulated ILW. It is therefore likely that the GDF may not be open for receipt of spent fuel until around 2075. Until then UK AGR SNF will be kept in interim wet storage in ponds at Sellafield, ultimately being consolidated into a single, long term storage pond. Specifically, in order to accommodate all future AGR SNF arisings until such time as a permanent disposal facility becomes available, a new racking system for the THORP Receipt and Storage pond has been proposed.

This new arrangement will mean that fuel will be packed closer together, the resultant increase in decay heat output causing a rise in the temperature of pond water from the 24°C that which obtains in the current storage arrangement. Present assessments indicate that rack water temperature could rise to approximately 60°C with an average of around 45°C [1].

The fuel is currently and will continue to be stored in interim storage ponds containing demineralized water with a chloride concentration typically < 0.1 ppm. AGR SNF storage ponds currently have a temperature of 24°C and a pH≈11.4, the latter achieved by dosing the pond with NaOH to inhibit corrosion. This storage regime has been shown to be effective for the safe storage of AGR fuel for up to ~25 years. Without such treatment, and specifically in the absence of NaOH as a corrosion inhibitor, cladding corrosion is observed, cladding perforation occurring within 1- 2 years in the presence of 0.2 – 0.3 ppm chloride in inhibitor-free / undosed pond water [2]. For higher chloride concentrations of 1-10 ppm, perforation was observed after only 100-200 days [2]. Cladding perforation is undesirable as it results in exposure of the spent fuel pellets to pond water and thus undesirable contamination of the pond with highly radioactive soluble fission products.

Current storage periods are typically less than 10 years, although this may extend to as long as 100 years after THORP closes. It is therefore necessary to determine whether AGR SNF can be stored safely in the same manner as it is currently without significant degradation of the SNF over this extended time scale.

The AGR fuel cladding will be in direct contact with

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the pond water, however in the case that the cladding is breached due to stress corrosion cracking, an unexpected rise in chloride levels or in the unlikely event that the cladding has been damaged during dismantling of the fuel assembly the fuel itself will be exposed to the pond water. Therefore, it is essential to study both the evolution of the cladding and fuel surfaces under pond water conditions.

The purpose of the work reported here is to establish a baseline corrosion behavior of AGR SNF in simulant pond water, through study of the corrosion of pure UO_2 and simulated AGR SNFs (AGR SIMFUELs) that have been especially fabricated for this work and whose development and characterization has been described previously, both in this issue and elsewhere [3-5].

2. Experimental

2.1. Materials

The UK National Nuclear Laboratory (NNL) fabricated UO_2 pellets and SIMFUEL pellets simulating AGR fuel pellet burn-ups of 25 GWd/tU and 43 GWd/tU. SIMFUEL pellets were prepared using sintering powder precursors containing the dopant compositions given in **Table 1**. The composition calculations were conducted using the FISPIN nuclear inventory calculation code (developed by NNL and distributed by AMEC [6]) and represent fuel pellets that have been aged for 100 years after removal from the reactor. A detailed description of the fabrication process and materials characterization of the pellets can be found in Hiezl *et al*. [3].

Table 1. Composition of AGR SIMFUEL pellets with different burn-ups.

Dopant	wt% 25GWd/tU	wt% 43GWd/tU
UO_2	95.705	92.748
Nd_2O_3	0.761	1.284
ZrO_2	0.793	1.276
MoO_3	0.614	1.027
RuO_2	0.512	0.892
$BaCo_3$	0.328	0.576
CeO_2	0.297	0.499
PdO	0.195	0.425
Rh_2O_3	0.080	0.115
La_2O_3	0.156	0.256
SrO	0.081	0.126
Y_2O_3	0.095	0.149
$CsCO_3$	0.311	0.495
TeO_2	0.073	0.130

Pond water simulants were prepared in doubly deionized water to the specification given in **Table 2** and dosed with hydroxide to a pH≈11.4 where appropriate. The simulant composition given in Table 2 is based on the average of sample data from the AGR storage pond which was analyzed once a week from October to December 2013. N.B. these values are those of the current AGR storage pond not the THORP Receipt and Storage pond. However, analysis of the

composition of the THORP pond during the same period suggests that use of the composition of Table 2 as a THORP pond water simulant would constitute a conservative approach.

Table 2. Simulant pond water composition.

Ion	Concentration /$\mu mol\ dm^{-3}$
Na^+	5.4×10^3
Ca^{2+}	2
Cl^-	30
SO_4^{2-}	2
K^+	5
OH^-	5.4×10^3

2.2. Electrode preparation

The UO_2 and SIMFUEL samples were mounted on brass bases and set in an epoxy resin mold to form a disk electrode. The surface of the sample was then polished using silicon carbide sandpaper (600 standard grit).

2.3. Electrochemistry

All electrochemical studies were carried out on a Metrohm Autolab potentiostat model PGSTAT128N using NOVA control and data acquisition software. A three-electrode cell was employed using a platinum mesh counter and a Ag/AgCl electrode as the reference electrode.

Cyclic voltammetry (CV) studies on UO_2 and SIMFUEL sample electrodes immersed in 0.5M Na_2SO_4 or pond water simulants were carried out at a scan rate of 10mV/s over a potential range of -1.8 to 0.4V. IR compensation was utilized during the voltammetric experiments on account of the resistive nature of UO_2 and SIMFUEL electrodes.

Open circuit potential (OCP) measurements on the three samples immersed in 0.5M Na_2SO_4, simulant pond water and a combination of 0.5M Na_2SO_4 and NaOH solution were carried out for a 12 hour period using a two electrode cell with a Ag/AgCl reference.

3. Results

In the first instance, to establish their baseline electrochemical behavior, CV experiments were carried out on the UO_2 and two SIMFUEL samples in 0.5M Na_2SO_4, pH≈5.6. These are shown in **Figure 1**, it is seen that the forward scans of each sample have three common peaks/regions. From the literature the origin of these peaks, seen in references [7,8], designated as peaks I to III with increasing applied potential, can be assigned as follows: peak I oxidation of UO_2 to UO_{2+x} at the grain boundaries; peak II oxidation of the bulk UO_2 matrix to UO_{2+x} with incorporation of O^{2-} ions into the lattice until a limiting stoichiometry of $UO_{2.33}$ is attained; peak III oxidation of UO_{2+x} to a U(VI) species such as soluble UO_2^{2+} or insoluble $UO_3 \cdot yH_2O$ [9].

It has been previously reported in work on LWR SIMFUELs that the addition of lower valence species, such as trivalent rare earths, causes an increase in the

electrical conductivity of the UO_2 bulk matrix. This is due to the ionization of uranium ions to maintain charge balance which creates mobile holes in the U 5f band. This allows for the passage of higher electrochemical currents though LWR SIMFUELs than pure UO_2 [10].

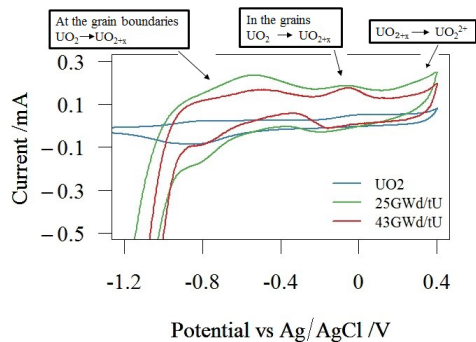Figure 1. Cyclic Voltammetry of UO_2, 25 and 43 GWd/tU SIMFUELs in 0.5M Na_2SO_4, pH≈5.6.

It can be seen from the CV results of Figure 1 that AGR SIMFUELs behave in a similar fashion. However, the currents associated with the higher burn-up SIMFUEL, 43 GWd/tU, are unexpectedly lower than those of the 25GWd/tU sample. It has been suggested by He *et al* that doping at higher lanthanide levels may stabilize the fluorite lattice against anodic oxidation and dissolution by decreasing the amount of vacancy sites free for O_2^- incorporation [11] – and it may be this stabilization that is responsible for the suppressed oxidation currents observed from the 43 GWd/tU sample compared to the 25 GWd/tU sample in Figure 1.
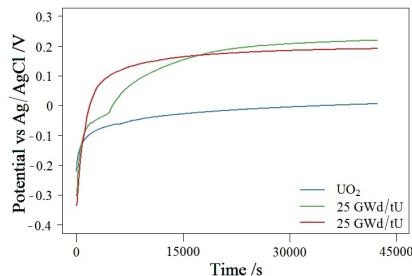

Figure 2. Open Circuit Potential measurements of UO_2, 25 and 43 GWd/tU SIMFUELs in 0.5M Na_2SO_4, pH≈5.6.

The OCPs for the UO_2, 25 GWd/tU and 43GWd/tU samples in 0.5M Na_2SO_4 at pH≈5.6 are observed to be 0.01V, 0.22V and 0.19V respectively as shown in **Figure 2**. If these values are compared to their positions on the CV in Figure 1 it is seen that the OCP of pure UO_2 sits on the anodic side of the current-voltage peak associated with the onset of the UO_2 to UO_{2+x} oxidation process.

However, the OCPs of both SIMFUEL samples are situated at the onset of the third peak/region where a U(VI) species is developing. Inspection of Pourbaix diagrams for the uranium-H_2O system (not shown) reveals that the OCPs of the SIMFUELs in the pH 5.6 Na_2SO_4 solution used in the experiments of Figures 1

and 2 lie in the potential region where the dissolution as UO_2^{2+} is expected to begin [12].

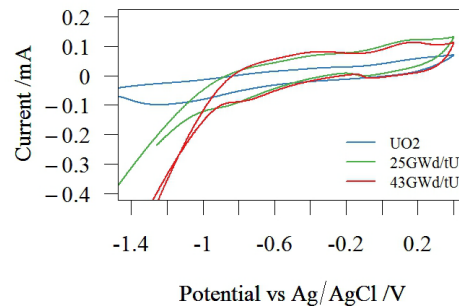Figure 3. Cyclic Voltammetry of UO_2, 25 and 43 GWd/tU SIMFUELs in simulant pond water.

The above baseline electrochemical experiments were then repeated in simulant pond water solutions of pH≈11.4, the results of the CV experiments being seen in **Figure 3**. Three common regions were observed in the forward-going sweeps of each voltammogram, which are attributed to the oxidation and dissolution of the surface with the same assignments as in Figure 1. The currents observed in Figure 3 are suppressed compared to those observed in Figure 1. It is possible that the currents are greater in Na_2SO_4 due in part to the development of local acidity as a result of hydrolysis of the UO_2^{2+} generated at positive potentials [11].

$$nUO_2^{2+} + yH_2O \rightarrow ((UO_2)_n(OH)y)^{(2n-y)+} + yH^+ \qquad (1)$$
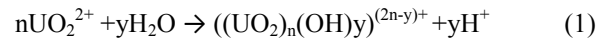
In the pH 11.4 simulant pond water, this acidity would be neutralized by the presence of the NaOH used as a corrosion inhibitor. Also in alkaline solution UO_2^{2+} has limited solubility and, again from inspection of the relevant Pourbaix diagrams, the U(VI) generated at higher potentials takes the form of insoluble $UO_3.yH_2O$ [11] which itself would be expected to precipitate as a current suppressing surface layer.
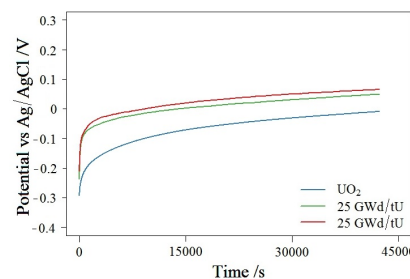

Figure 4. Open Circuit Potential measurements of UO_2, 25 and 43 GWd/tU SIMFUELs in simulant pond water, pH≈11.4.

A reduction in the OCPs is also observed under pond water conditions (pH≈11.4), the values recorded for pure UO_2, 25GWd/tU and 43GWd/tU being -0.01V, 0.05 and 0.06V respectively, as shown in **Figure 4**. On inspection of the CVs of these samples in simulant pond water shown in Figure 3 it can be seen that the OCP of pure UO_2 again sits at the onset of the current peak associated with the onset of the UO_2 to UO_{2+x} oxidation process – whereas the OCPs of both SIMFUEL samples sit on

anodic side of this same wave (i.e. towards potentials where the oxidation to UO_{2+x} will be more advanced). Therefore, the OCPs for both SIMFUELs in alkaline pond water lie at potentials negative of those seen in near-neutral Na_2SO_4 solutions (see Figure 2) and in the region where a potentially protective UO_{2+x}–type oxide layer is growing on the surface of the sample.

To show the direct implications of the effect of NaOH and pH, the OCPs were measured for a 0.5M Na_2SO_4 solution dosed with NaOH to pH≈11.4 see **Figure 5** from which it can be seen that the equilibrium OCPs for pure UO_2, 25 and 43GWd/tU samples are -0.06V, 0.04 and 0.06 respectively. These values are almost identical to those found for simulant pond water at the same pH as shown in Figure 4. These values for UO_2, 25 and 43GWd/tU samples are all more negative than the analogous readings recorded in neutral electrolyte, Figure 2, illustrating how increasing the pH decreases the OCPs of all three samples. The equilibrium OCPs recorded from the 25 and 43 GWdtU samples in neutral media in Figure 2 lie on the wave associated with matrix oxidation to UO_2^{2+} in Figure 1. In contrast, the analogous OCPs recorded in pH 11.4 media in Figures 4 and 5 lie at potentials more negative than those where dissolution as UO_2^{2+} would be expected in Figure 3, suggesting that the presence of NaOH at pH 11.4 suppresses the dissolution as UO_2^{2+}.

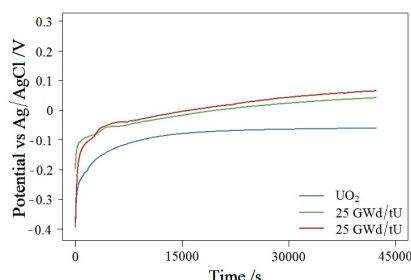Figure 5.   Open Circuit Potential measurements of UO_2, 25 and 43 GWd/tU SIMFUELs in 0.5M Na_2SO_4 dosed to pH≈11.4 with NaOH.

4. Conclusions

These studies report the voltammetric behavior of pure UO_2 and AGR SIMFUELs in simulant pond water (pH≈11.4) and compares these results to their behavior in a simple electrolyte, 0.5M Na_2SO_4, of pH≈5.6. The most significant observations are as follows:

- There are lower corrosion currents for all three samples in simulant pond water compared to those seen in the Na_2SO_4 solution.
- There is a reduction in the OCP for all samples under pond water conditions. Particularly, the OCP for the SIMFUEL samples moves from a region where active dissolution of the surface may be expected to an area where an oxide layer is developing. It is likely that this oxide layer then protects the surface from dissolution.

These experiments provide preliminary indications that dosing the pond water to a pH of ~11.4 provides corrosion protection. Future work will include a series of electrochemical impedance spectroscopy and Raman microspectroscopy studies to elucidate the nature of the above-mentioned protective oxide, and the conducting of analogous experiments on real irradiated fuel at Sellafield to assess how good an analogue these SIMFUELs are for real spent nuclear fuel.

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