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EXPERIMENTS***

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I. INTRODUCTION

Unsaturated drip tests have been used to investigate the alteration of unirradiated UO₂ and spent UO₂ fuel in an unsaturated environment, such as may be expected in the proposed repository at Yucca Mountain.^{1,2} In these tests, simulated groundwater is periodically injected onto a sample at 90°C in a steel vessel. The solids react with the dripping groundwater and water condensed on surfaces to form a suite of U(VI) alteration phases. Solution chemistry is determined from leachate at the bottom of each vessel after the leachate stops interacting with the solids. A more detailed knowledge of the compositional evolution of the leachate is desirable. By providing just enough water to maintain a thin film of water on a small quantity of fuel in batch experiments, we can more closely monitor the compositional changes to the water as it reacts to form alteration phases.

II. EXPERIMENTAL DESIGN

Batch experiments are conducted at 90°C. Each reaction vessel consists of a 45 mL stainless-steel (SS) pressure vessel and lid, inside of which is a SS hanger and SS screen. In each experiment, ~0.2 g of UO₂ is used such that O₂ consumption during oxidative corrosion of UO₂ does not limit the reaction.

The solid is unirradiated UO₂, the same material used in drip experiments on UO₂.^{1,3} A unit-cell refinement on X-ray diffraction (XRD) data of the starting material gives a unit-cell constant, $a = 0.547(1)$ nm, consistent with stoichiometric UO₂. Solid UO₂ was ground by hand under ethanol in an agate mortar and pestle and sieved to separate the particle-size fraction of 75 to 45 μm. Four experiments, PDT-3 through PDT-6, were performed with as-sieved UO₂ powder; and two experiments, PDT-7 and PDT-8, used powder rinsed with ethanol to remove fine particles.

Approximately 0.5 mL of EJ-13 water³ was added to each reaction vessel. The estimated solid-surface-area to solution-volume (S/V) of these experiments is 5000 m⁻¹ (assuming 45 μm -diameter UO₂ spheres). Two experimental series were performed (Table 1). Three experiments used unmodified EJ-13 water and ran 28 to 114 days. To address the role of radiolytic products on increasing the oxidation potential in solution, three experiments used EJ-13 water with 0.1 mol L⁻¹ H₂O₂ {"EJ-13(ox)"}; these experiments ran 35 to 70 days.

After each run, solution pH was measured at room temperature. Solution aliquots were passed through a 0.45 μm filter (except PDT-4 and PDT-6), and all solutions were acidified to pH ≅ 1 with HNO₃. Solutions were analyzed by inductively coupled plasma - mass spectrometry (ICP-MS). Reacted powders were air dried and examined by optical microscopy, scanning electron microscopy (SEM) with energy dispersive x-ray spectrioscropy (EDS), and XRD.

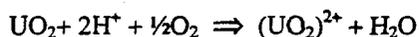
III. RESULTS

Experiments with EJ-13(ox) have higher measured [U] than experiments with unmodified EJ-13 (Table 1). The two experiments for which solutions were not filtered (PDT-4 and PDT-6, "uF" in Fig. 1) have the highest measured [U] and represent maximum concentrations of dissolved U. Solution pH tends towards lower values as the reaction progresses (Fig. 1). Solution pH of experiments with EJ-13(ox) are lower than for experiments with unmodified EJ-13. Figure 1 illustrates the observed variation in solution [U] and pH as a function of reaction progress. Except for PDT-5, [U] decreases with increasing pH (Table 1; Fig. 1).

We observed solid U(VI) alteration products in five experiments (Table 2). Uranyl silicates formed only in experiments that lasted 70 days or more, although no uranyl silicates were observed in the longest-run experiment (PDT-5, 114 days). Dehydrated schoepite (DS) precipitated in the three experiments with added H₂O₂, whereas metaschoepite (MS) formed in only one experiment, PDT-5, which used unmodified EJ-13.

IV. DISCUSSION

Reactions most relevant to the chemical evolution of the water are oxidation and dissolution of U⁴⁺ in UO₂ and Fe⁰ in steel, as well as precipitation of U, Si, Na, and Fe. A reaction of particular interest is oxidative dissolution of solid UO₂. In acidic solution, this is:



Dissolution of UO_2 is enhanced at low pH in the presence of O_2 (or other oxidant). Note that the concentration of dissolved U is negatively correlated with pH (Fig. 1)

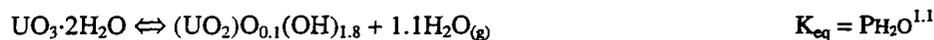
Precipitation of U(VI) alteration phases is pH dependent. Relevant reactions include precipitation of MS, DS and soddyite, possibly uranophane and compreignacite (Table 2). No Na-bearing U(VI)-alteration phases were identified, consistent with results from drip tests on unirradiated UO_2 , in which only minor Na-U phases are formed. In contrast, drip experiments on spent UO_2 fuel are dominated by Na-uranyl silicate formation. The chemical evolution of EJ-13 water contacting spent UO_2 fuel may be more complex than changes occurring in experiments on unirradiated UO_2 .

Steel corrosion can decrease solution pH due to precipitation of ferric oxy-hydroxides, which were observed in all experiments. Experiments that used 304L-SS screens had slightly higher pH values, probably owing to greater corrosion resistance (Table 1). Co-precipitation of U with Fe oxides has been reported for natural and experimental systems.^{4,5,6} We did not detect U in Fe-oxide precipitates examined by SEM/EDS.

We expect that H_2O_2 in EJ-13(ox) decomposes in steel vessels at 90°C . One-half mole of O_2 is produced for each mole of H_2O_2 decomposed, increasing the partial pressure of oxygen ($p\text{O}_2$) in the vessel 6%. This may seem a small change, but the effects are significant. Total [U] increased more rapidly and remained higher in experiments with EJ-13(ox); pH values of EJ-13(ox) leachates are lower (Table 1). Every experiment with EJ-13(ox) precipitated U(VI) alteration products, and DS precipitated only in experiments with EJ-13(ox).

The formation of DS in only those experiments with EJ-13(ox) may be explained by higher $p\text{O}_2$.

Equilibrium between MS and DS is



Dehydrated schoepite is stable with respect to MS for $p\text{H}_2\text{O} < 0.527$ atm at 25°C .⁷ Metaschoepite alters to DS in water near 100°C .⁸ As 90°C is close to the transition temperature for 100 % humidity ($p\text{H}_2\text{O} = 1$ atm), a 6% increase in $p\text{O}_2$ may decrease $p\text{H}_2\text{O}$ enough to stabilize DS. Increased $p\text{O}_2$ also enhances steel corrosion; this probably explains lower pH values for EJ-13(ox) leachates than for EJ-13 leachates (Table 1).

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Table 1. Experimental Details

Test ID	Screen Stainless Steel	Water*	UO ₂ mass (g)	EJ-13 mass (g)	Run Time (d)	Reaction Progress (d·m ⁻¹)	solution pH (25 °C)	solution [U] _{tot} (mg L ⁻¹)
PDT-3	316	EJ-13	0.2005	0.50	28	140,000	5.8	36.9
PDT-5	316	EJ-13	0.1986	0.50	114	570,000	4.4	> 10
PDT-7	304L	EJ-13	0.2004	0.50	74	370,000	6.1	15.4
PDT-4	316	EJ-13 (ox)	0.2003	0.51	35	175,000	4.5	3920
PDT-6	316	EJ-13 (ox)	0.2006	0.49	70	350,000	4.6	717
PDT-8	304L	EJ-13 (ox)	0.1994	0.50	70	350,000	5.0	71.3

* EJ-13 is unmodified EJ-13 water; EJ-13(ox) indicates EJ-13 with 0.1 mol L⁻¹ H₂O₂.

Table 2. Solid U(VI)-Bearing Alteration Products Tentatively Identified in High S/V Batch Tests

Solid Phase*	Ideal Formula	Experiment ID
dehydrated schoepite	(UO ₂)O _{0.25-x} (OH) _{1.5+2x} (0 ≤ x ≤ 0.15)	PDT-4, PDT-6, PDT-8 (?)
metaschoepite	UO ₃ ·2H ₂ O	PDT-5
compreignacite (?)	K(UO ₂) ₃ O ₂ (OH) ₃ (H ₂ O) ₄	PDT-8
soddyite	(UO ₂) ₂ (SiO ₄)(H ₂ O) ₂	PDT-6
uranophane (?)	Ca(UO ₂) ₂ (SiO ₃ OH) ₂ (H ₂ O) ₅	PDT-7
swamboite (?)	U ⁶⁺ (UO ₂) ₆ (SiO ₃ OH) ₆ (H ₂ O) ₃₀	PDT-7

* All phase identifications based on SEM/EDS only. A question mark indicates uncertain identification.

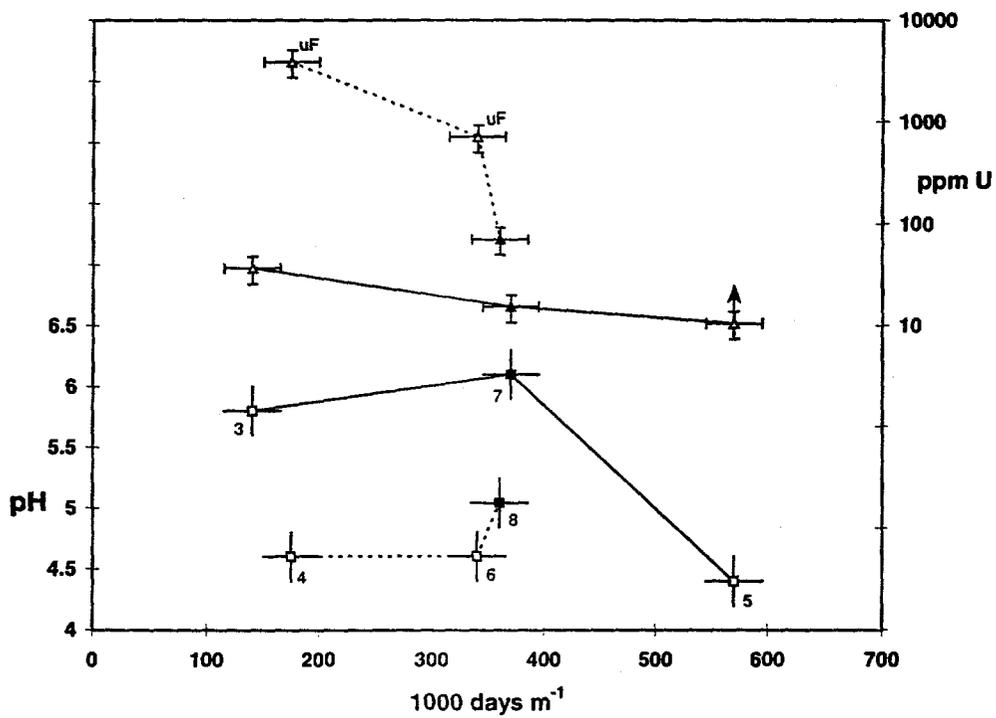


Figure 1: Variation of [U] and pH with reaction progress. Dotted lines represent experiments with EJ-13(ox); a "uF" denotes unfiltered solutions (PDT-4, PDT-6) and represent *maximum* [U] values; the arrow indicates the *minimum* [U] value (PDT-5). Open-ended error bars denote pH values; closed-ended error bars are for [U] values (symbolism for clarity only). Filled symbols denote tests with 304L-SS screens (PDT-7, PDT-8).