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CONCENTRATION OF URANIUM AND PLUTONIUM IN UNSATURATED SPENT FUEL TESTS

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1. Introduction

Commercial spent fuel is being tested under oxidizing conditions at 90°C in drip tests with simulated groundwater to evaluate its long-term performance in a potential repository at Yucca Mountain [1-4]. The tests allow us to monitor the dissolution behavior of the spent fuel matrix and the release rates of individual radionuclides. This paper reports the U and Pu concentrations in the leachates of drip tests during 3.7 years of reaction. Changes in these concentrations are correlated with changes in the measured pH and the appearance of alteration products on the fuel surface. Although there is little thermodynamic information at 90°C for either uranyl or plutonium compounds, some data are available at 25°C [5-8]. The literature data for the U and Pu solubilities of U and Pu compounds were compared to the U and Pu concentrations in the leachates. We also compare Wilson's [9] U and Pu concentrations in semi-static tests at 85°C on spent fuel with our results.

2. Experimental Description

The experimental setup for these unsaturated tests, which are done with the uranium oxide fuels, ATM-103 and ATM-106, has been reported elsewhere [1]. The burnups are 30 MW•d/kg U for ATM-103 and 45 MW•d/kg U for ATM-106. The leachant, EJ-13, is a dilute sodium carbonate solution saturated with silica. In the tests, ~0.75 mL of the EJ-13 is dripped on the spent fuel samples held at 90°C. The leachate is analyzed ~ every six months.

3. Results and Discussion

The measured U and Pu concentrations in the leachate during the drip tests are shown in Figs. 1 and 2 for ATM-103 and ATM-106, respectively. In both tests, the U and Pu concentrations decreased as reaction time increased. After 3.7 years of reaction, the U

and Pu concentrations in the ATM-106 test are an order of magnitude lower than those in the ATM-103 test. The leachate pH dropped from the original 8.5 of the leachant to 4-6 at 0.3 years. Thereafter, the pH increased and was 7.3 after 3.7 years of reaction.

^{238}U - The highest U concentrations ($\sim 10^{-5}$ M) in both tests were measured within the first 0.3 years of reaction. At 1.6 years in the ATM-103 test, we noted yellow nucleation sites on the spent fuel surfaces, which might indicate that a specific uranium phase was forming. At 3.7 years, the alteration products on the two fuels were examined. The phases Na-boltwoodite, $\text{Na}(\text{UO}_2)(\text{SiO}_3\text{OH})\cdot\text{H}_2\text{O}$, and β -uranophane, $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2\cdot 5\text{H}_2\text{O}$, were identified as the major alteration phases in the ratio of 80:20, respectively [4]. At 3.7 years, the U concentration was 4×10^{-7} and 3×10^{-8} M for ATM-103 and ATM-106, respectively.

Figure 3 shows the U concentration at 90°C as a function of pH after 0.3, 1.6, and 3.7 years of reaction for both fuels. Wilson [9] reported a ^{238}U concentration of 6×10^{-7} M at pH -8 in the leachant J-13, an unmodified form of EJ-13; this concentration is also plotted in Fig. 3. Wilson noted that uranophane was indicated as an alteration product from x-ray diffraction results.

The experimental data in Fig. 3 are plotted on a diagram that was calculated for the dominant uranium phases and/or aqueous species at equilibrium at 25°C as a function of pH. The equilibrium data at 25°C were used since data at 90°C do not exist for most uranium phases. The U concentrations were calculated for a fixed EJ-13 leachant, atmospheric CO_2 ($p_{\text{CO}_2} = 10^{-3.5}$), and atmospheric O_2 . (The calculated values were derived from the program Geochemist's Workbench, which incorporates the data of Grenthe et al. [5] and Nguyen et al. [6].) In these diagrams, multiple uranium phases can be present at a given pH at 25°C even at equilibrium conditions, but only the dominant phase is usually shown.

We represent three cases in Fig. 3. In case (a), uranophane is the dominant phase between pH 5 and 12, and soddyite is the dominant phase below pH 5. In cases (b) and (c) the data for uranophane were suppressed so that other phases that were present could be plotted. In case (b), Na-boltwoodite is the dominant phase between pH

7 and 10, and soddyite is the dominant phase below pH 7. In case (c), the data for Na-boltwoodite and soddyite were suppressed. The dominant phase is then becquerelite above pH 7.5, and meta-schoepite below pH 7.5. (No error bars are shown on the calculated portion of the diagram but, if shown, the boundaries of each of the phases would change by ~ 0.5 pH unit.) We would expect similar equilibrium diagrams if the data at 90°C were available, but the position of each phase would be shifted to higher U concentrations and different pHs.

These diagrams can be used to examine the correlation between the experimental U concentrations and the dominant solid phases identified at a given reaction time. The two data points at pH 7 correspond to the U concentrations after 3.7 years of reaction for ATM-103 and ATM-106 when Na-boltwoodite and β -uranophane were the major phases present. Thus, the experimental results are consistent with the concentrations expected from the equilibrium diagram.

^{239}Pu - For ^{239}Pu , the highest concentrations (10^{-7} to 10^{-8} M) also occurred within the first 0.3 years of reaction. [The ^{239}Pu concentration is about 50% of the total Pu (^{239}Pu , ^{240}Pu , etc.)] As reaction time increased, the Pu concentration decreased and was of the order of 10^{-10} M after 3.7 years of reaction for the two drip tests. The Pu concentrations after 0.3, 1.6, and 3.7 years of reaction are plotted as a function of pH in Fig. 4, as is Wilson's ^{239}Pu data point for his 85°C test [9].

The experimental data in Fig. 4 are plotted on a diagram that was calculated for the dominant plutonium phases and/or aqueous species at equilibrium at 25°C as a function of pH. The equilibrium data at 25°C were used since data at 90°C do not exist for plutonium phases. The Pu concentrations were calculated for a fixed EJ-13 leachant, atmospheric CO_2 ($p_{\text{CO}_2} = 10^{-3.5}$), and atmospheric O_2 . (The calculated values were derived from the program Geochemist's Workbench, which incorporates the data of Rai et al. [7] and Rai and Swanson [8].) Two cases are shown in Fig. 4. In case (a), PuO_2 is the dominant phase. In case (b), the data for PuO_2 were suppressed. The dominant phase is then $\text{PuO}_2(\text{OH})_2$. Similar diagrams would be expected if the data at 90°C were available.

The experimental data points suggest that the Pu that is released from spent fuel may be in equilibrium with PuO_2 . However, since some of the reacted Pu may be retained on the spent fuel in a uranium-plutonium-molybdenum-zirconium oxide, which is like the phases identified in uranium-plutonium oxide fuels, e.g., $(\text{Ba,Sr,Cs})(\text{U,Pu,Zr,Mo})\text{O}_3$ [10], the use of an equilibrium diagram may have limited use in predicting the progress of Pu release.

4. Conclusions

We found that the U and Pu concentrations were consistent with those expected from equilibrium diagrams for phases expected in spent fuel tests. This may have been fortuitous, but, it may also be an indication that the steady-state conditions in drip test are not far from equilibrium conditions. Unsaturated drip testing of these fuels will continue.

5. References

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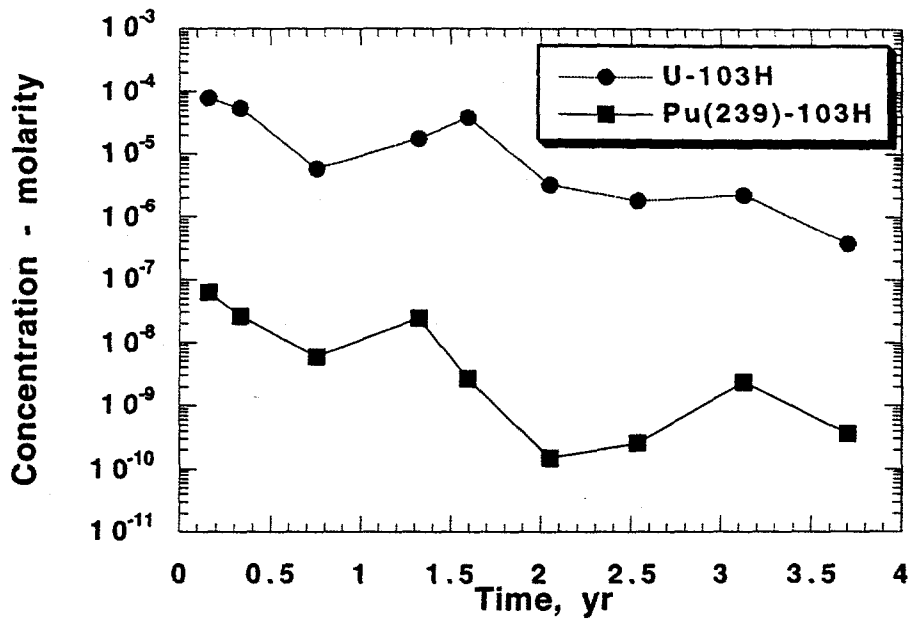


Fig. 1. Uranium and Plutonium Concentration in the Drip Test with ATM-103.

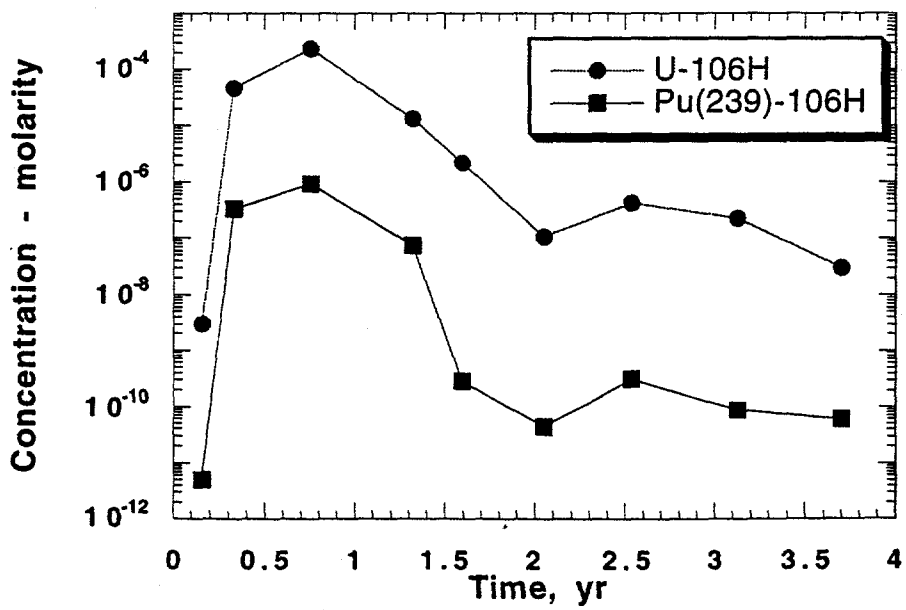


Fig. 2. Uranium and Plutonium Concentration in the Drip Test with ATM-106.

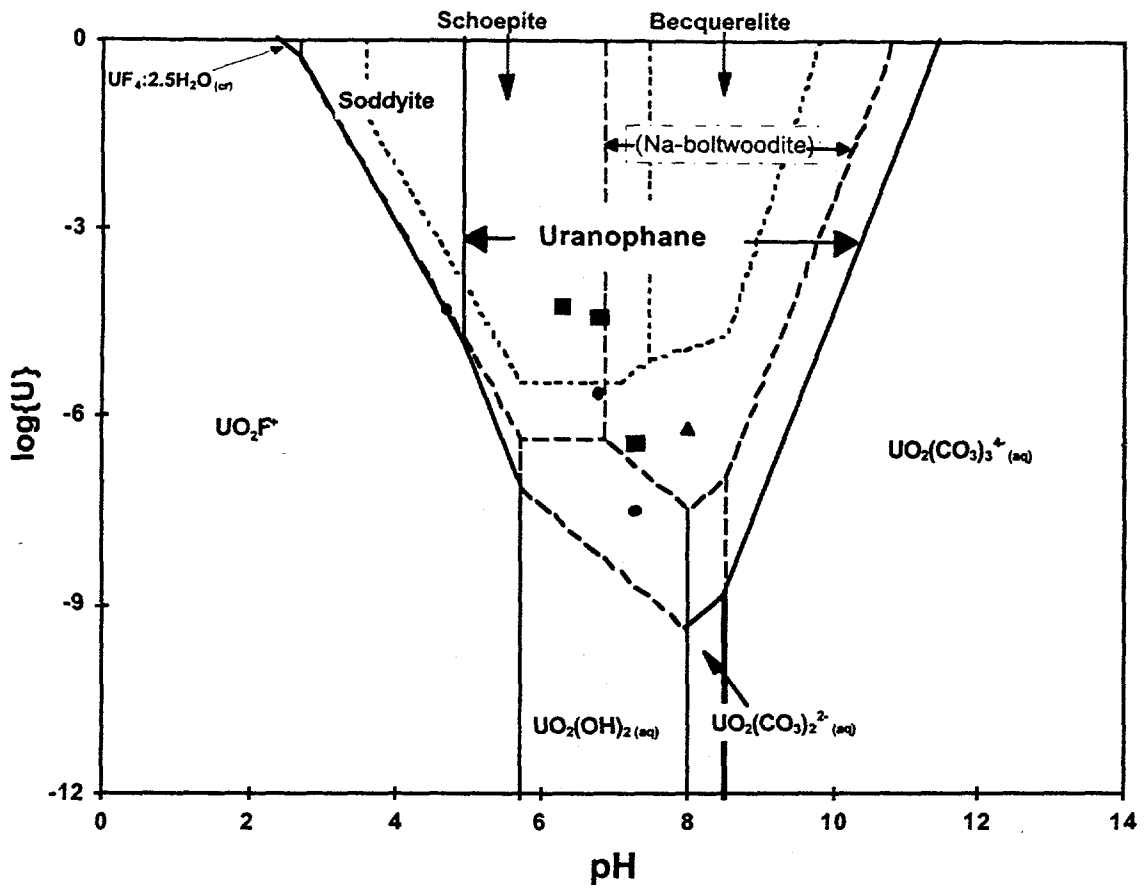


Fig. 3. The Log of the Uranium Concentration (M) at 90°C in Drip Tests for ATM-103 (squares) and ATM-106 (circles) as a Function of pH. Also plotted are the U concentrations at 25°C for known uranium solids. The triangle is Wilson data point.

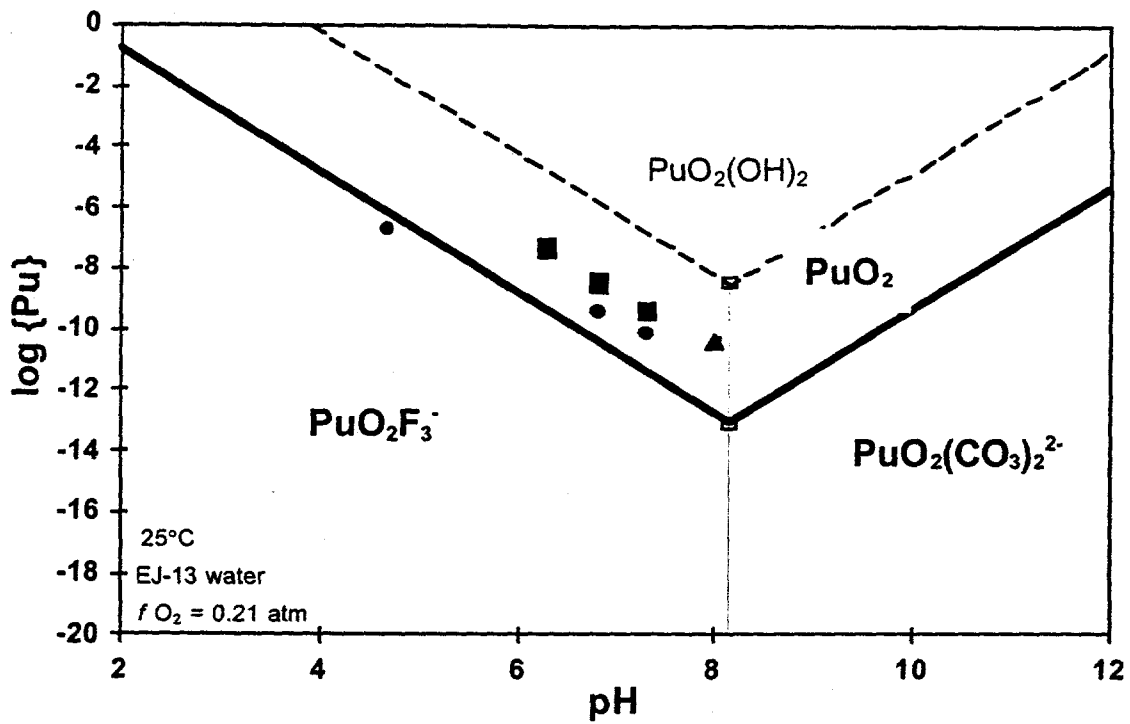


Fig. 4. The Log of the Plutonium Concentration (M) at 90°C in Drip Tests for ATM-103 (squares) and ATM-106 (circles) as a Function of pH. Also shown are the Pu concentrations at 25°C for known plutonium solids. The triangle is Wilson's data point. (The assumed conditions for the Pu calculations are shown in the lower left hand corner of the figure.)