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LEACHING OF UO₂

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Eh AND FISSION PRODUCT SOLUBILITIES;*

TWO FACTORS IN THE LEACHING OF UO₂

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Abstract

Eh was found to have a large effect on the dissolution of UO_2 in water at pH 4. As was estimated from thermodynamic data, the solubility was found to decrease and become very low as the oxygen fugacity, and therefore the Eh of the water, was decreased. Some of the rare earths and other actinides such as europium, cerium, americium, and plutonium released during the leaching of a spent fuel element behaved differently. These elements were not affected to any large extent by the variation in Eh of these experiments. It has been postulated that these elements reached their solubility limits and precipitated as the spent fuel was leached.

Although crystalline UO_2 may or may not be the waste form of greatest potential, the leaching of UO_2 can yield information that is applicable to other waste forms.

It has been stated many times that the solubility of UO_2 should be extremely low in neutral pH water in the absence of all oxygen. Based on the data and estimates collected by Langmuir(1) the concentration of uranium in equilibrium with crystalline and amorphous UO_2 have been calculated as a function of pH and several low oxygen fugacities. The curves generated from these calculations are shown in Figure 1. In these curves the concentration of uranium decreases rapidly as the pH is increased from 0 to 4 and then increases as the pH is further increased to 14. At an oxygen fugacity of 10^{-83} atm, the point where water is in equilibrium with 1 atm of hydrogen gas, the concentration of uranium at pH 4 is less than 0.01 ppb if the crystalline form of UO_2 is in equilibrium with the water.

We have attempted to measure the solubility under such conditions. A two liter polypropylene container was filled with deionized water and purged with hydrogen gas in the presence of platinum gauze. Powdered UO_2 that was 7% ^{235}U was added and the solution was continuously stirred and purged by recirculating hydrogen gas. Periodically the Eh and pH were measured without exposing the solution to air and small samples were taken for uranium analysis. An Eh of -180 mv. was measured throughout most of the experiment implying a very low oxygen fugacity of 10^{-80} atmospheres in the solution.

Figure 2 is a plot of the uranium concentration in solution as a function of time. The concentration of uranium after the first 15 days

is a value that is 10^7 higher than expected from the thermodynamic estimates. One must conclude either that the estimates are very wrong or the oxygen content of the water is still quite high.

On the 84th day of the experiment palladium black, as a catalyst, was added to the system to speed up, if possible, the reaction of the hydrogen purge gas with any oxygen still in the water. The effect was dramatic and the concentration of uranium in solution decreased rapidly to ~100 ppb; a result that is still high but much closer to the thermodynamic estimates. If the experiments were continued for longer times perhaps the equilibrium value would be attained.

Various conclusions can be made from the preceding results that are appropriate not only to UO_2 as a nuclear waste form but also to other waste forms.

As one would estimate from thermodynamic data the solubility of UO_2 is indeed dependent on the oxygen concentration of the leachant and decreases as the oxygen concentration is decreased. However, it is difficult to produce solutions of very low oxygen concentration. The practice of bubbling an inert gas or hydrogen through a solution really is not an acceptable manner for producing low oxygen fugacities. For example, if the purging gas has ~0.01 ppm oxygen in it the equilibrium concentration of oxygen in the solution will be 3.5×10^{-7} ppm or 2.5×10^{-10} atmospheres. In comparison to the oxygen fugacities needed for low UO_2 solubilities shown on Fig. 1 this concentration of oxygen is not very low.

It has also been shown that a measured negative Eh of a solution does not necessarily mean a low oxygen concentration. The oxygen reaction at an electrode is too slow and irreversible for the measured Eh to be a true indication of oxygen concentration in the solution.

We have also studied the solubility of H. B. Robinson spent fuel elements in deionized water. The experimental conditions of the IAEA leach test were essentially followed except that the atmosphere was controlled in and above the leachant as a method of varying the Eh of the solution(2). Oxidizing conditions were established by purging the leachant with CO₂-free air, and a somewhat reducing condition by purging with 6% hydrogen - 94% argon gas.

If the process of dissolution of spent fuel element is congruent dissolution of the matrix UO₂, the ratios of the fission-product rare earths and actinides to uranium should be approximately the same for the leachant as for the original spent fuel. Table 1 is a list of these ratios for a 14 day leaching at 25°C and a 35 day leaching at 70°C under both oxidizing and somewhat reducing conditions.

Note the large difference between the spent fuel and leachant ratios at 70°C under oxidizing conditions. The decrease in the ratio can be brought about by decreasing concentrations of the rare earths and actinides or by increasing uranium concentrations in the leachant. In fact, both conditions were observed. A more extensive description of the differences in concentration of uranium and the rare earths and actinides with time can be found in Reference(2) and also the proceedings of the 1980 Materials Research Society Meeting(3). Saturation of the leachant

by these elements and subsequent precipitation of some form of hydrous oxide was used as an explanation of the data. Solubilities calculated from the results are listed in Table 2. Note that there apparently is a negative temperature coefficient of solubility for these precipitates. These results are averages of the experiments in oxidizing and reducing atmospheres since the results differed by less than a factor of 10 for all elements except uranium. At 70°C the higher value for uranium is under oxidizing conditions.

The results illustrate that the solubilities in water of some of the rare earths and actinides are low at slightly acid pH's. Care must be taken in planning and executing experiments where the concentration of these elements may be at or near these levels. A question also arises on some of the standard leach tests as to the validity of assuming that everything that leaves the bulk waste form is on its way to the biosphere. These rare earth and actinide precipitates are "in situ" alternate waste forms in themselves.

Captions

Fig. 1. Solubility of UO_2 in Water as a Function of pH and $f(O_2)$

Fig. 2. Time Dependence of Uranium Concentration

TABLE 1. Element to Uranium Ratios

TABLE 2. Solubilities at pH 4, Deionized Water

UO₂ UO₂A

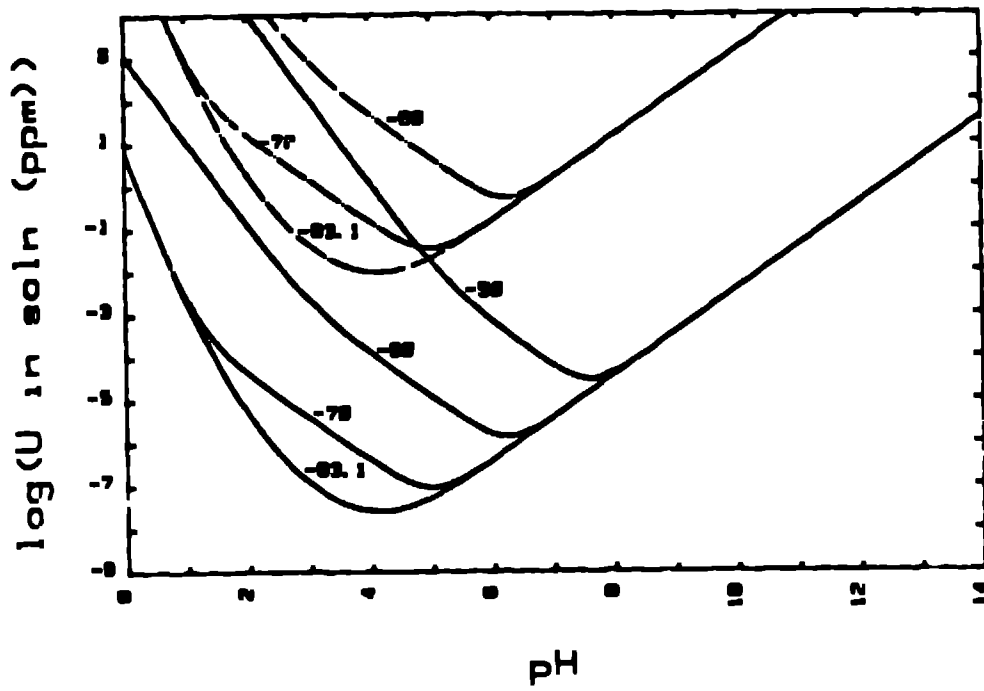


FIG. 1. Solubility of UO₂ in water as a function of pH and p(O₂)

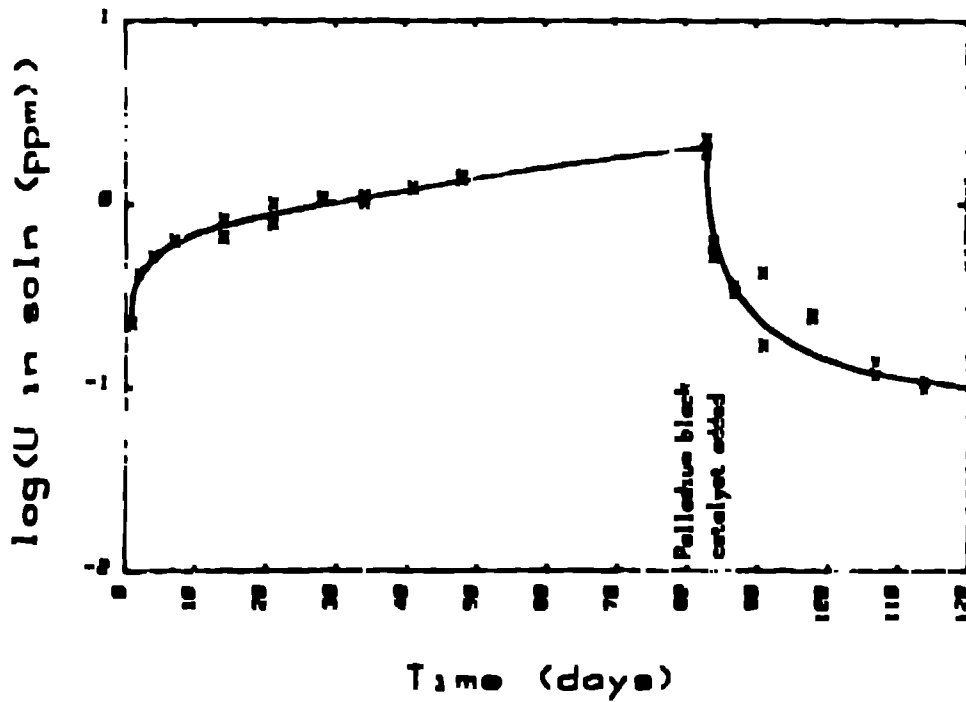


FIG. 2. Time Dependence of Uranium Concentration.

TABLE 1
ELEMENT TO URANIUM RATIOS
REDUCING CONDITIONS

Eu	Ce	Am	Pu	
Leachant				
1.6 E-4	2.3 E-3	2.2 E-4	1.1 E-4	25°C
1.6 E-4	1.7 E-3	2.7 E-4	3.5 E-3	70°C
Fuel Element				
1.9 E-4	3.6 E-3	5.0 E-4	1.3 E-2	
OXIDIZING CONDITIONS				
Leachant				
1.7 E-3	9.9 E-3	1.4 E-3	7.9 E-3	25°C
5.8 E-4	3.2 E-5	~ 3 E-6	1.7 E-5	70°C

Note: Computer notation used in the Tables, 2.0 E-5 = 2.0×10^{-5} .

TABLE 2
SOLUBILITIES AT pH 4, DEIONIZED WATER

Element	25°C	70°C
Eu	2.4 E-8M	2 E-9M
Ce	3 E-7	1 E-8
Am	25 E-8	2 E-9
Pu	3 E-7	1 E-8
U	25 E-5	2.3 E-4 ~2 E-6

REFERENCES

- 1) D. Langmuir, "Uranium Solution-Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits," *Geochimica et Cosmochimica Acta*, 42: 547, (1978)
- 2) A. E. Norris, "Fission Product Release," ONWI/Sub/80/E511-01200-7, (1980)
- 3) A. Ogard, G. Bentley, E. Bryant, C. Duffy, J. Grisham, E. Norris, C. Orth, and K. Thomas, "Are Solubility Limits of Importance to Leaching?" Proceedings of the 1980 Materials Research Society Meeting, Boston