Corrosion Mechanisms of Spent Fuel under Oxidizing Conditions

P. A. Finn, R. Finch, E. Buck, J. Bates

Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439-4837

ANL/CMT/CP-93030

CONF-970902--

RECEIVED

OCT 24 1997

OSTI

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

Submitted

Materials Research Society

September 27, 1997

* This work was performed under guidance of the Yucca Mountain Site Characterization Project (YMP) and is part of activity D-20-43 in the YMP/Lawrence Livermore National Laboratory Spent Fuel Scientific Investigation Plan. This work was supported by the U.S. Department of Energy under contract W-31-109-ENG-38.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Corrosion Mechanisms of Spent Fuel under Oxidizing Conditions

P. A. Finn, R. Finch, E. Buck, J. Bates
Argonne National Laboratory, Argonne, IL 60439 USA

ABSTRACT

The release of ^{99}Tc can be used as a reliable marker for the extent of spent oxide fuel reaction under unsaturated high-drip-rate conditions at 90°C . Evidence from leachate data and from scanning and transmission electron microscopy (SEM and TEM) examination of reacted fuel samples is presented for radionuclide release, potential reaction pathways, and the formation of alteration products. In the ATM-103 fuel, 0.03 of the total inventory of ^{99}Tc is released in 3.7 years under unsaturated and oxidizing conditions. Two reaction pathways that have been identified from SEM are 1) through-grain dissolution with subsequent formation of uranyl alteration products, and 2) grain-boundary dissolution. The major alteration product identified by X-ray diffraction (XRD) and SEM, is Na-boltwoodite, $\text{Na}[(\text{UO}_2)(\text{SiO}_3\text{OH})]\cdot\text{H}_2\text{O}$, which is formed from sodium and silicon in the water leachant.

INTRODUCTION

To predict the behavior of spent oxide fuel in an oxidizing environment, an understanding of its corrosion behavior and the associated release of long-lived radionuclides is needed. To accomplish this, commercial spent oxide fuel is being reacted under oxidizing conditions at 90°C in drip tests with simulated groundwater and in vapor tests to evaluate its long-term behavior in a potential repository at Yucca Mountain. The tests monitor the dissolution behavior of the spent fuel matrix and the release rate of individual radionuclides.

The objective of this paper is to provide data about the reaction of spent oxide fuel (ATM-103 and ATM-106) under oxidizing and unsaturated conditions. Data that identify the alteration products are presented along with the leachate fractional releases of ^{99}Tc , ^{238}U , ^{239}Pu , ^{137}Cs and ^{97}Mo for both fuels. This information is used to discern the processes by which spent oxide fuel is reacting.

EXPERIMENTAL

The two pressurized-water-reactor fuels used are ATM-103, which has a burnup of 30 (MW·d)/kg U [1], and ATM-106, which has a burnup of 43 (MW·d)/kg U [2]. The fuel samples, 7-8.5 g total, are in the form of individual fragments weighing 0.3 to 1.2 g each. The average geometric surface area for both fuels is $2.1 \times 10^{-4} \text{ m}^2/\text{g}$. The measured [3] ^{99}Tc distribution in the two fuels is $<0.1\%$ in the gap and grain-boundaries and $>99\%$ in the fuel matrix.

The leachant came from well J-13 near Yucca Mountain, which has a chemistry representative of the saturated zone below Yucca Mountain, Nevada. Before use it was equilibrated for eighty days at 90°C with crushed core samples of Topopah Spring tuff. It is designated EJ-13. Sampling procedures, drip rates, and the conditions for the vapor tests have been noted previously [4].

After 3.7 and 4.1 years of reaction fuel fragments were examined by scanning and transmission electron microscopy (SEM and TEM). The removed fragment is rolled on tape to collect alteration products and small pieces of fuel with alteration products attached. This process results in the removal of some of the porous alteration products. Parallel electron energy loss spectrometry (EELS) was used to obtain actinide M-edges [5]. For the ATM-103 high drip rate test, X-ray powder diffraction (XRD) data was used to confirm the identity of the alteration phases.

The term "interval" for the leachate data refers to the time between sequential samplings of the leachate. The "interval release fraction" for a given radionuclide is defined as the ratio (R/T) where R is the amount of radionuclide collected in a given interval, i.e., the total amount in the leachate and the acid strip, and T is the amount of radionuclide calculated [1,2] to be in the fuel. Since material incorporated into alteration products, adsorbed on the Zircaloy sample holder, and

on the spent fuel is not included, the radionuclide with the largest interval release fraction provides a minimum estimate of the spent fuel reaction rate. The interval release fractions are used to compare releases for different radionuclides for the same reaction interval and for the same radionuclide for different reaction intervals. A "cumulative release fraction" is the sum of the individual interval release fractions over a total fuel reaction time.

RESULTS

We report three sets of results 1) radionuclide release into the leachate, 2) corrosion of ϵ -phase intermetallic particles composed of Ru-Mo-Tc-Rh-Pd as seen by TEM examination, and 3) corrosion of the UO_2 matrix as noted from SEM examination. The three sets of results provide a picture of extensive corrosion of the spent fuel in a short time (3.7 years).

Leachate Results - The use of the ^{99}Tc release fraction as a marker for the minimum extent of the spent fuel reaction (minimum since there may be some Tc hold up in alteration products) has been proposed [6]. The ^{99}Tc interval release fraction has been relatively constant over 3.7 years of reaction of the high-drip-rate tests for ATM-103 fuel (Fig. 1) and from 1.3 to 3.7 years of reaction for ATM-106 fuel (Fig. 2). Also shown in Fig. 1 and Fig. 2 are the interval release fractions for ^{238}U and ^{239}Pu . The decrease in the U and Pu release fractions after 1.6 years of reaction is apparent in both figures.

Fig. 1. ATM-103 High-Drip-Rate Test: ^{99}Tc , ^{238}U , and ^{239}Pu Interval Release Fractions.

In Table I, the cumulative release fractions for ^{99}Tc , ^{238}U , and ^{239}Pu , as well as for ^{137}Cs and ^{97}Mo are shown for several cumulative reaction times. Table I illustrates the following points. First, after 3.7 years of reaction, the cumulative ^{99}Tc release fractions for the two fuels are comparable, 0.03 of the total inventory for ATM-103 and 0.02 for ATM-106. Second, for the ATM-103 fuel, the ^{97}Mo cumulative release fraction after 3.7 years of reaction is comparable to the ^{99}Tc cumulative release fraction; however, for the ATM-106 fuel, the ^{97}Mo release fraction is only 10% of the ^{99}Tc release fraction. Thus, some of the Mo appears to be held up in the ATM-106 test; however, at 4.1 years of reaction, the Mo and Tc release fractions appear comparable (data analysis is still in progress). Third, the ^{137}Cs cumulative release fractions for the two fuels are comparable but are only 10-20% of the cumulative ^{99}Tc release fraction. It appears that most of this ^{137}Cs is

held up. An alteration product that can incorporate both Cs and Mo is $(\text{Cs}_{0.9}\text{Ba}_{0.55})[(\text{UO}_2)_5(\text{MoO}_2)\text{O}_4(\text{OH})_6] \cdot 6\text{H}_2\text{O}$ [7]. The formation of this alteration product could

Fig. 2. ATM-106 High-Drip-Rate Test: ^{99}Tc , ^{238}U , and ^{239}Pu Interval Release Fractions.

account for the hold up of ^{137}Cs and Mo relative to ^{99}Tc , especially in the ATM-106 test prior to 4.1 years of reaction. Fourth, prior to the first 1.6 years of reaction, both fuels had a large ^{238}U release fraction (Fig. 1 and 2), but thereafter, most (99.9%) of the reacted uranium remained on the fuel surface in alteration products based on the difference in release fractions between ^{99}Tc and U, the visual appearance of the fuel, and the weight gain measured. Fifth, prior to the first 1.6 years of reaction, both fuels had a ^{239}Pu release fraction that was equivalent to 10-40% of the U release fraction. At longer reaction times, most of the Pu was held up. (See Fig. 1 and 2).

The picture of corrosion provided by the leachate data for both fuels is one in which there is a continuous release of ^{99}Tc over four years of reaction, consisting of 10^{-3} of the total inventory in each six-month interval. The U release effectively ceases after a year's reaction, but large amounts of uranium appear to be incorporated into alteration products that form on the fuel surface. Their formation accelerated after 1.6 years of reaction, but the ^{99}Tc release was not affected. The ^{99}Tc release fraction can be used to calculate the fraction and thus the amount of uranium that has reacted and this value can be compared to the amount of sodium and silicon removed from the dripped EJ-13 water. In addition, the weight gain for the reacted spent fuel can be compared to the expected increase in weight for the formation of different alteration products. These data are summarized in Table II for the two fuels after 3.1 years of reaction. (Units of moles are used for simplicity in comparing the different elements.)

The major alteration product in the high-drip-rate tests was determined to be Na-boltwoodite on the basis of SEM and XRD evidence. Some of the excess uranium is assumed to be incorporated into dehydrated schoepite on the basis of its identification in the vapor test [8]. Other alteration products present include the Cs-bearing uranyl molybdenum-oxyhydroxide.

TEM Examination of ϵ -Phase Particles - Microtomed samples of reacted fuel were examined to determine if the ϵ -phase particles (Ru-Mo-Tc-Rh-Pd) were being oxidized as proposed [6]. Table III shows the distribution of the five elements in unreacted fuel and the ratio Mo/(Ru+Pd), which can range from 0.9 to 1.5, depending on fission yield [1] or the distribution found in unreacted fuel [1]. To determine if the ϵ -phase particles had reacted in both the ATM-103 high-drip-rate and the vapor tests, the Mo/(Ru+Pd) ratio was measured in reacted particles, as was

the change in the relative amounts of the five elements in the ϵ -phase particles.

Table I. Cumulative Release Fractions^a for the High-Drip-Rate Tests

Time (yr)	⁹⁹ Tc	⁹⁷ Mo	¹³⁷ Cs	²³⁸ U	²³⁹ Pu
1.6 Years of Reaction					
ATM-103	2.1E-2 ^b	1.9E-3	1.8E-3	8.6E-5	9.8E-6
ATM-106	1.6E-3	8.5E-4	3.0E-3	1.8E-4	1.4E-4
2.5 Years of Reaction					
ATM-103	2.4E-2	2.6E-3	2.0E-3	9.0E-5	9.9E-6
ATM-106	9.6E-3	1.0E-3	3.4E-3	1.8E-4	1.4E-4
3.1 Years of Reaction					
ATM-103	2.9E-2	1.4E-2	3.7E-3	9.2E-5	1.0E-5
ATM-106	1.7E-2	.8E-3	4.0E-3	1.8E-4	1.4E-4
3.7 Years of Reaction					
ATM-103	3.0E-2	1.6E-2	4.7E-3	9.3E-5	1.0E-5
ATM-106	2.0E-2	2.1E-3	5.0E-3	1.8E-4	1.4E-4

^a Cumulative release fractions have been rounded to two significant figures.

^b The unit E-2 is 1×10^{-2} .

Table II. High-Drip-Rate Tests - Alteration Products after 3.1 Years of Reaction

Species	Na- Boltwoodite ^c mol	Dehydrated Schoepite ^d mol	Unknown Compound ^e mol	Total mol	Calculated ^a Weight-UO ₂ g	Measured ^b Weight Gain g
ATM-106					0.07	0.06
U	2.9E-4	6E-5	1E-4	4.5E-4		
Si	2.9E-4	---	---	2.9E-4		
Na	2.9E-4	---	6E-4	8.9E-4		
ATM-103					0.07	0.05
U	2.7E-4	2E-4	2.9E-4	8E-4		
Si	2.7E-4	---	---	2.7E-4		
Na	2.7E-4	---	1E-5	2.8E-4		

^a Difference between sum of masses of alteration products and the original fuel's UO₂.

^b Difference between original fuel weight and that after 3.1 years of reaction. The weight gain for the interval between 2.5 and 3.1 years was estimated as the average over the previous 2.5 years: 0.01 g/0.5 yr for ATM-106 and 0.007 g/0.5 yr for ATM-103. Weights when water was retained were not used.

^c Formula: Na[(UO₂)(SiO₃OH)] • H₂O. This was the major alteration product from XRD; the silicon was assumed to be primarily in this product. The total moles of uranium are based on the ⁹⁹Tc release fraction.

^d Formula: UO₃ • 0.8 H₂O. This was identified in the vapor test.

^e The moles listed are the difference from the total moles.

Table III. Composition of Reacted ϵ -Phase Particles in ATM-103 Tests (elements in wt%)

Unreacted Particles					
Element	Fission Yield ^a	Grain[1] Boundary	Grain[1]		
Mo	40	39.9	52		
Tc	10	11.8	8		
Ru	30	42.3	23		
Rh	5	5.6	6		
Pd	15	0.4	12		
Mo/(Ru+Pd)	0.9	0.9	1.5		
High Drip Rate Test after 3.7 Years of Reaction					
Element	Edge Region	Pit Region	Pu-Rich ^b Region		
Mo	12.3	16.6	15.2		
Tc	5.0	10.1	3.9		
Ru	41.7	44.8	45.1		
Rh	7.5	17.6	9.8		
Pd	32.6	10.8	26.1		
Mo/(Ru+Pd)	0.2	0.3	0.2		
Vapor Test after 4.1 Years of Reaction					
Mo	29	30	30	29	26
Tc	9	12	11	17	15
Ru	40	30	30	33	42
Rh	-	-	-	-	-
Pd	22	28	28	22	17
Mo/(Ru+Pd)	0.5	0.5	0.5	0.5	0.4

^a This is the average distribution in the fuel.

^b Quantification of EELS was done using a 100 eV window and the oscillator strength values calculated from a Dirac-Fock model.

Three locations in the TEM sample were examined to find ϵ -phase particles that had not totally reacted in the high drip rate test. The regions are designated edge, dissolution pit, and Pu-rich region. The edge region refers to a location on a reacted fuel grain. The dissolution pit was an area in which only reacted ϵ -phase particles were found. The Pu-rich region was one in which the Pu concentration was 20 times greater than that expected from the amount of burnup in the fuel. (In Fig. 3, the TEM/EELS spectrum at the U-M absorption edge shows the Pu increase in an area in which spent fuel has reacted. A similar buildup in Pu concentration for reacted fuel has been found in the ATM-103 vapor test.) In all three regions in the high-drip-rate test (see Table III), the ϵ -phase particles have reacted in a similar fashion, i.e., the Ru and Rh content was greater than that in the unreacted phase and the particles have a new composition in which the Mo/(Ru+Pd) ratio is 0.2 to 0.3. In both the edge region and the Pu-rich region, there was a significant decrease in the Tc and Mo concentrations, but an increase in the Pd concentration. Thus, ϵ -phase particles that have not totally reacted (i.e., disappeared from the fuel) are depleted in Tc and Mo.

Fig. 3. ATM-103 High Drip Rate Test after 3.7 Years of Reaction: Concentration of Pu (Pu-M₅ peak) in Unreacted Fuel (minor peak) and in Reacted Fuel (large peak).

In the ATM-103 vapor test after 4.1 years of reaction, several reacted ϵ -phase particles were examined (see Table III). All had a Mo/(Ru+Pd) ratio that was lower than that for the unreacted particle, i.e., 0.4 to 0.5 versus 0.9 and had also retained more Mo than had those in the high-drip-rate test, i.e., about 80% more based on the Mo/Ru ratio.

SEM Examination of the ATM-103 Fuel - High-Drip-Rate Test - As one reacted fuel fragment in the ATM-103 high-drip-rate test was examined after 3.7 years of reaction, it disintegrated into individual grains and clumps of grains. This suggested that reaction had occurred along all of the grain boundaries throughout the fuel fragment. A piece of this friable fragment was polished and then examined with SEM. Based on crystal morphology, chemical composition (EDS), and XRD, the most abundant (~80%) alteration product was Na-boltwoodite, $\text{Na}[(\text{UO}_2)(\text{SiO}_3\text{OH})] \cdot (\text{H}_2\text{O})$. Additional minor phases were detected by TEM and XRD analyses, including beta-uranophane, $\text{Ca}[(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2] \cdot 5(\text{H}_2\text{O})$ (~10 vol%). (From TEM/EELS analysis, both Mo and Ru were found at levels of 1-3 wt% in the beta-uranophane product.)

In Fig. 4, a cross section through one piece of the reacted ATM-103 fragment is shown. Gaps of $\leq 0.5 \mu\text{m}$ between the fuel grains are visible in the brightest region in the image. No alteration phases were detected between the grain boundaries, nor was Si evident in the grain boundaries from EDS. (TEM examination of the edges of the fuel grains found no evidence for oxidation of UO_2 to $\text{UO}_{2.25}$.)

Surrounding the fuel is an alteration layer (~20-40 μm thick) consisting predominantly of Na-boltwoodite. This layer consists of two regions: a dense inner layer, 5-10 μm thick, closest to the fuel surface and a porous outer layer, 10-30 μm thick. No difference in composition is evident between the two layers from EDS. Near the outer edge of the dense inner layer is an interface defined by a gap (i.e., a dark band) that lies approximately 10 μm above the fuel surface and 2-3 μm below the outer edge of the dense layer. Below the gap, crystals of Na-boltwoodite have formed more or less perpendicular to the fuel surface, whereas above the gap, Na-boltwoodite forms a dense mat of crystals sub-parallel to the fuel surface. Above these flat lying crystals is the porous outer layer. As the fuel dissolved, Na-boltwoodite replaced the fuel at the surface uniformly inward from the original outer surface without regard to grain boundaries.

Figure 4. (a) Cross Section through a Reacted Fragment of ATM-103 after 3.7 Years of Reaction. Brightest area is fuel grains with grain boundary gaps. Medium contrast is Na-boltwoodite. Darkest contrast is epoxy. (b) A magnified view of the right side of (a). (c) A magnified view of left side of (a).

DISCUSSION

We have [6] suggested that the dissolution of spent fuel is controlled by the oxidizing effect of the products of alpha radiolysis of the thin film (<10 nm [9]) of water at the fuel surface [10]. The oxidants also facilitate oxidation and dissolution of the ϵ -phase particles. Since the ϵ -phase particles are homogeneously dispersed in the ATM-103 fuel matrix [1], the rate of matrix dissolution should govern their rate of exposure to the oxidizing environment, and, consequently, the ^{99}Tc release fraction should reflect the minimum matrix dissolution rate.

In the ATM-103 high-drip-rate test, 0.03 of the total ^{99}Tc inventory has been released after 3.7 years of reaction. This release has occurred in steady increments, which suggests either that the reaction pathways have been constant during this time or that the contribution from multiple reaction pathways has not varied over time. From mass balance considerations, i.e., the depletion of sodium and silicate from the EJ-13 leachant, the fraction of uranium that could react to form Na-boltwoodite is comparable to the fraction of ^{99}Tc that has been released. The change in composition of partially reacted ϵ -phase particles are consistent with the leachate data, i.e., that the ϵ -phase particles are reacting as the spent fuel dissolves, leaving behind Rh and Pd.

The SEM data for the ATM-103 high drip rate sample provides insight into the possible reaction pathways that contribute to matrix dissolution. The two pathways seen in Fig. 4 are

through-grain dissolution and grain-boundary dissolution. A third pathway that could contribute is the dissolution of micro-grains within the grain boundaries.

The configuration of the alteration products leads us to believe that the dense inner layer represents a region in which the spent fuel has been replaced more or less by Na-boltwoodite. The gap, which is ~10 μm above the fuel surface in the image, is interpreted as corresponding to the position of the original surface of the unreacted fuel.

In Fig. 4c, the thickness of the dense layer is $\leq 5 \mu\text{m}$ at the extreme left corner, which suggests that replacement is not isovolumetric. However, to obtain an estimate of the maximum amount of spent fuel that would have reacted by through-grain dissolution, one can use the average thickness of the reacted layer (10 μm) and assume that replacement is 100% volumetric. The maximum amount of reacted fuel is then 0.023 of the total mass of uranium in the test given a geometric surface area of $2.1 \times 10^{-4} \text{ m}^2/\text{g}$ and an ~8-g sample. However, since there is about a four-fold volume increase from cubic UO_2 to monoclinic Na-boltwoodite, only 25% of the uranium in the replaced fuel layer can be incorporated by the Na-boltwoodite within the dense inner layer. The remaining 75% of the uranium would be transported out of this layer. Of this latter amount, up to half can be accounted for by the outer porous layer of Na-boltwoodite. The other half may be accounted for by (1) the portion of the alteration layer that was lost in preparing the SEM sample, (2) the nonuniform thickness of the alteration layer noted in visual examinations, and (3) the amount of alteration phases that have collected in the base of the Zircaloy fuel holder (noted but not measured).

Dissolution also occurred along grain boundaries, as evident from the friable nature of the fuel fragment and the wide gaps found between grains (Fig. 4). The minimum extent of the grain-boundary reaction can be estimated by subtracting the maximum extent of through-grain reaction (0.023) from the cumulative ^{99}Tc release fraction (0.03); this minimum is 0.007 of the total mass. Through-grain dissolution of the UO_2 fuel matrix appears to predominate over grain boundary dissolution, since the surface area of fuel reacted along grain boundaries is quite large compared to a uniform ~10- μm -thick surface replacement layer. Thus, as the grain boundaries opened, the ^{99}Tc release fractions should have increased if grain boundary dissolution predominated.

The formation of Na-boltwoodite at the fuel surface suggests that subsequent to matrix dissolution, uranium ions in solution coprecipitate with the sodium (Na^+) and the silicon (H_4SiO_4) in the water. A simple equation that accounts for oxidative dissolution of the UO_2 fuel by an oxidizing source (represented by O), and the subsequent formation of Na-boltwoodite is:

As Na- and Si-rich EJ-13 water is added to a system with an oxidizing source, the net replacement reaction proceeds to the right. The effects of other reactions have not been considered.

CONCLUSIONS

The solids characterization of the spent oxide fuel surface after 3.7 years of reaction at 90°C under unsaturated and oxidizing conditions at a high-drip-rate suggests that the spent fuel rapidly reacts by two pathways, through-grain dissolution with formation of alteration products and a slower grain boundary dissolution. As the fuel reacts, the ϵ -phase particles react releasing ^{99}Tc ; the major alteration product formed is Na-boltwoodite. Elements other than uranium, including Ru, Mo, Cs, and Ba, are incorporated into the (U^{6+}) alteration products.

ACKNOWLEDGMENTS

This work was performed under the guidance of the Yucca Mountain Site Characterization Project (YMP) and is part of activity D-20-43 in the YMP/Lawrence Livermore National Laboratory Spent Fuel Scientific Investigation Plan. The work is supported by the U.S. Department of Energy under contract W-31-109-ENG-38.

REFERENCES

1. R. J. Guenther et al., Characterization of Spent Fuel Approved Testing Material - ATM-103, Pacific Northwest Laboratory Report PNL-5109-103 (1988).
2. R. J. Guenther et al., Characterization of Spent Fuel Approved Testing Material - ATM-106, Pacific Northwest Laboratory Report PNL-5109-106 (1988).
3. W. J. Gray, D. M. Strachan, and C. N. Wilson, Mater. Res. Soc. Symp. Proc. **257**, 353 (1992).
4. P. A. Finn, E. C. Buck, M. Gong, J. C. Hoh, J. W. Emery, L. D. Hafenrichter, and J. K. Bates, Radiochimica Acta, **66/67**, 189 (1994).
5. E.C. Buck and J.A. Fortner, Ultramicroscopy **67**, 69-75 (1997).
6. P.A. Finn, J.C. Hoh, S. F. Wolf, M. T. Surchik, E. C. Buck, and J. K. Bates, Mater. Res. Soc. Symp. Proc. **465**, 527-534 (1997).
7. E. C. Buck, D. J. Wronkiewicz, P. A. Finn, & J. K. Bates, accepted J. Nucl. Mater. (1997).
8. E. C. Buck, R. J. Finch, P. A. Finn, and J. K. Bates, this proceeding.
9. J. Hagymassy, S. Brunauer, and R. Sh. Mikhail, J. Coll. Inter. Sci. **29**, 485 (1969). On powdered materials at 100% RH, six monolayers of water (each 0.3 nm) were observed to sorb.
10. D. W. Shoesmith, S. Sunder, L. H. Johnson, and M. G. Bailey, Mater. Res. Soc. Symp. Proc. **50**, 309-316 (1985).