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**INITIAL RESULTS FROM DISSOLUTION TESTING
OF VARIOUS AIR-OXIDIZED SPENT FUELS**

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INITIAL RESULTS FROM DISSOLUTION TESTING OF VARIOUS AIR-OXIDIZED SPENT FUELS

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ABSTRACT

Flowthrough dissolution tests have been conducted on two different light-water-reactor spent fuels oxidized to U_4O_{9+x} or U_3O_8 . Oxidation had a bigger impact on the dissolution of U and a smaller impact on the dissolution of Tc from the fuel with higher burnup and higher fission gas release. Possible reasons for the observed differences in test results are discussed, but clarification awaits results from tests on other fuels, which are in progress.

INTRODUCTION

Yucca Mountain, Nevada, is being evaluated as a potential geologic repository site for spent nuclear fuel. This site, which is in the unsaturated zone above the water table, is relatively dry and in equilibrium with atmospheric air. If spent fuel were placed in this site, it would not be contacted by water during the first several hundred years after disposal while waste package temperatures exceeded 95°C, the boiling temperature of water at the repository elevation. However, if a waste container and fuel cladding both failed, the fuel could be contacted and oxidized by moist air at a rate and extent dependent upon the fuel temperature following the container and cladding failures. At temperatures below about 200°C, the oxidation would probably be limited to the formation of U_4O_{9+x} ^(a). At higher temperatures, more extensive oxidation to produce U_3O_8 or even $UO_3 \cdot xH_2O$ could occur. The purpose of this work is to investigate the stability toward dissolution by groundwater of each of these more highly oxidized phases of spent fuel.

Data presented in an earlier paper¹ showed that, for the one type of spent fuel tested, the intrinsic dissolution rate (i.e., the U dissolution rate per unit surface area of sample) of the fuel oxidized to U_4O_{9+x} was similar to that of unoxidized fuel. Although oxidation had a minor effect on the U dissolution rate, more recent results indicated an order of magnitude increase in the initial rate that Tc dissolved after the spent fuel was oxidized to U_4O_{9+x} . This led to speculation that the large difference in Tc dissolution rates for oxidized versus unoxidized spent fuel was associated with the ϵ -phase (Mo-Tc-Ru-Rh-Pd solid solution alloy) particles that have been observed in all light water reactor spent fuels.² The enhanced Tc dissolution from oxidized fuel, it was speculated, may involve two prerequisites: 1) the grain-boundary cracking that accompanies formation of U_4O_{9+x} and exposes the metallic ϵ -phase particles that lie preferentially along the grain boundaries and 2) the surfaces of the ϵ -phase particles along the cracked grain boundaries may oxidize and consequently increase the Tc solubility.

It was also speculated that oxidation of spent fuel to U_3O_8 might further enhance the initial dissolution of soluble radionuclides. When UO_2 is oxidized to U_3O_8 , a large increase in surface area occurs because of extensive inter- and intra-granular cracking that accompanies the large decrease in density. It was speculated that the cracks may intercept some of the fission gas bubbles, which are present throughout the UO_2 matrix.³ If that occurs, fission products such as Cs and I, which may be associated with gas bubbles, would become more accessible for

(a) LWR spent fuel oxidized in air at 110 to 200°C approaches a stoichiometry of $-UO_{2.4}$, but has the cubic crystal structure of U_4O_9 .²

dissolution. In addition, the Tc-containing metal particles, which are also associated with gas bubbles,³ would be made more accessible to water.

An exploratory testing program has been started in which spent fuel is being oxidized to U_4O_{9+x} and U_3O_8 , and the initial dissolution rates of soluble radionuclides are being measured along with the intrinsic dissolution rates of U. Results from the first portion of this testing program are reported here.

EXPERIMENTAL

Test specimens were prepared from the two fuels listed in Table I. Both fuels were oxidized to U_4O_{9+x} as previously described,^{1,2} and both were also tested in as-received (unoxidized) condition. Both oxidized (U_4O_{9+x}) and unoxidized specimens were prepared in two forms, particles and grains.¹ "Particle" specimens consisted of hundreds (~1 g) of 700- to 1,700- μ m particles, each particle containing several thousand grains. "Grain" specimens consisted of many thousands (~0.1 g) of separated grains from 7 to 20 μ m in size.

One test specimen consisted of ATM-106 spent fuel oxidized to U_3O_8 . It was prepared by heating previously unoxidized particles ~1 mm in size at 430°C in air for 18 hours. X-ray powder diffraction (XRD) measurements confirmed that the specimen was essentially 100% U_3O_8 with no extra lines observed in the XRD pattern.

Table II summarizes the characteristics of all of the test specimens and the solutions used to test them.

Table I. Characteristics of Spent Fuels

<u>Fuel</u>	<u>Type</u>	<u>Burnup</u> <u>(MWd/kgM)</u>	<u>Fission Gas Release</u> <u>(%)</u>	<u>Reference</u>
ATM-105	BWR	31	0.6	4
ATM-106	PWR	50	18	5

The good agreement between surface areas determined by particle-size-distribution and BET measurements noted in Table II (Note c) applies only to grain specimens. The surface areas determined by both of these methods is thought to be a reasonable representation of the surface that is accessible to water because the grain specimens contain few small cracks or pores that would be inaccessible to water. On the other hand, BET measurements of the particle specimens overestimate the effective surface area because most of the internal grain boundary surfaces measured by the BET method are inaccessible to water. Therefore, BET measurements were not used for the particle specimens. This is further discussed in the following section.

Dissolution rates were measured for the specimens listed in Table II using a flowthrough system with test solution flow rates typically ~12 mL/h.¹ Note that the test solutions listed in Table II for the ATM-105 and ATM-106 fuels were slightly different, but previous measurements¹ have shown that this changes dissolution rates by a factor of only about two.

Table II. Test Specimen Characteristics and Test Conditions

<u>Fuel</u>	<u>Type</u>	<u>Oxidation State</u>	<u>Specimen Size (g)</u>	<u>Surface Area (cm²/g)</u>	<u>Test Conditions</u>
ATM-105	Grains	UO ₂	0.15	980 (a)	(d)
		U ₄ O _{9+x}	0.15	910 (a)	(d)
	Particles	UO ₂	1.3	17 (a)	(d)
		U ₄ O _{9+x}	1.1	15 (a)	(d)
ATM-106	Grains	UO ₂	0.064	2,770 (b)	(e)
		U ₄ O _{9+x}	0.22	1,150 (b, c)	(e)
	Particles	UO ₂	1.2	19 (a)	(e)
		U ₄ O _{9+x}	0.94	22 (a)	(e)
	Powder	U ₃ O ₈	0.019	4,900 (b)	(e)

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- (a) Calculated from particle-size distribution measurements.¹
 (b) Measured by the BET method.
 (c) Surface areas of 860 cm²/g and 1,150 cm²/g were determined by particle-size distribution and BET measurements, respectively. This was considered good agreement. See discussion in text.
 (d) Test solution was 2 x 10⁻³ M NaHCO₃/Na₂CO₃, 50°C, pH = 8.8 (after calculated temperature correction), equilibrated with air containing 120 ppm CO₂ to stabilize the pH.
 (e) Test solution was 2 x 10⁻² M NaHCO₃, 25°C, pH = 8.0, equilibrated with air containing 11,000 ppm CO₂ to stabilize the pH.

RESULTS AND DISCUSSION

Figures 1 and 2 show dissolution rates for oxidized (U₄O_{9+x}) and unoxidized (UO₂) ATM-106 and ATM-105 fuel, respectively. Figure 3 presents dissolution rate data for ATM-106 fuel oxidized to U₃O₈. Five major conclusions can be drawn from these data. First, based on U data, ATM-106 fuel dissolved faster when oxidized to U₄O_{9+x} than it did in unoxidized (UO₂) form (Figure 1). This was unlike ATM-105 fuel, which dissolved at about the same rate in both U₄O_{9+x} and UO₂ forms (Figure 2). Second, Figures 1 and 2 show a significant difference in the behavior of Tc between ATM-105 and ATM-106 fuel. Third, Figure 3 shows an initially high dissolution rate of Cs from ATM-106 fuel oxidized to U₃O₈, resulting in the release of 12% of the total Cs inventory during the first day. Fourth, data presented in Figure 3 show a surprisingly low Tc dissolution rate, apparently resulting from oxidation of ATM-106 fuel to U₃O₈. Fifth, implications regarding UO₂ oxidation/dissolution mechanisms can be derived from the U data shown in Figures 1-3. Each of these conclusions is discussed separately below along with some related minor points. Note that the U and Cs data presented in Figure 2 were published earlier¹ and are included here for completeness.

Comparison of U₄O_{9+x} and UO₂ Spent Fuel Dissolution Rates

The first major conclusion drawn in the preceding paragraph will be further described here by the discussion of three points: 1) oxidation had little effect on the dissolution rates of ATM-105 fuel grain or particle specimens, but a more pronounced effect on ATM-106 grains and particles; 2) the increase in dissolution rates, due to oxidation, was about twice as much for particles as for grains with both ATM-105 and ATM-106 fuels, which suggests that oxidation

exposed more surface by partially opening the grain boundaries of the particle specimens; and 3) particles *apparently* dissolved faster than grains for both ATM-105 and ATM-106 fuels. This is an artifact of the surface area measurement methods used, and it allowed an estimate to be made of the depth to which grain boundaries were penetrated by water during these tests.

The first point compares the U dissolution rates of oxidized versus unoxidized specimens for two spent fuels. Figure 1 shows that oxidized ATM-106 fuel grains dissolved about 5 times faster than unoxidized grains and that oxidized ATM-106 fuel particles dissolved about 10 times faster than unoxidized particles. This contrasts with the data in Figure 2, which shows that oxidation to U_4O_{9+x} had little effect on the dissolution rate of ATM-105 fuel grains and only a modest effect on the dissolution rate of particles. The major differences between the two fuels are that ATM-106 fuel had a higher burnup and a higher fission gas release. Higher burnup is probably relatively unimportant because its effect is primarily to increase the inventory of fission products. High gas release seems more likely to correlate with dissolution behavior because it is indicative of elevated operating temperatures near the center of the fuel with corresponding grain growth and precipitation or migration of fission products. However, additional fuels must be tested to determine whether the effect of oxidation can be generally correlated with fission gas release and associated microstructural changes.

The second point is most readily observed in Figure 1 where oxidation is shown to have had twice as much effect on the dissolution rate of the ATM-106 fuel particles as it had on the grains. That is, oxidation produced a 5-fold increase in the U dissolution rate of ATM-106 fuel grains (compared to unoxidized grains) and about a 10-fold increase for particles. This suggests that oxidation opened the grain boundaries of the particles and allowed water to penetrate to a depth about twice that of the unoxidized particles. This result is similar to that observed with the ATM-105 particles (see Figure 2 and ref. 1).

The third point involves the comparison of U dissolution rates from particles versus grains for both oxidized and unoxidized test specimens; particles *apparently* dissolved faster than grains. It is important to recognize that intrinsic dissolution rates must be independent of specimen morphology and that the *apparent* difference occurs only because of differences in the way the surface areas were measured for the grain and particle specimens. As described below, this *apparent* difference was used to estimate the depth to which the water penetrated the grain boundaries of the particle specimens during these tests.

Particle surface-area measurements are inherently ambivalent. The BET method seriously overestimates the effective surface area because it includes a large portion of the internal grain boundary surfaces that are not open to penetration by water. In contrast, the geometric method used to estimate the surface areas of the particle specimens¹ assumes that *none* of the grain boundaries are exposed to water. In reality, a small portion of the grain boundaries clearly are penetrated by water.^(a) Thus, the geometric method actually underestimates the effective surface area of the particle specimens somewhat.

Grain specimen surface areas measured by the BET method are thought to be reasonable representations of the surfaces actually exposed to water, as discussed in the Experimental Section. Therefore, the dissolution rates shown in Figures 1 and 2 for the grain specimens are expected to be true intrinsic rates.

Since true intrinsic dissolution rates of particles and grains must be equal, the *apparent* difference between particles and grains shown in Figures 1 and 2 must be due to the exposed grain-boundary surfaces of the particles that were not accounted for by the geometric surface-area measurement method. Thus, the 5-fold difference in grain and particle dissolution rates (Figure

(a) In this view, essentially 100% of the grain boundaries that intersect the surfaces of a particle are penetrated by water to a depth of one, or a few, grain diameters. However, grain boundaries in the interior of the particle are not penetrated. Thus, only a "small portion" of the total volume of grain boundaries in a particle are penetrated by the water.

2) was used to estimate¹ that the outer two or three layers of grain boundaries of the ATM-105 particle specimens were exposed to water. By similar argument, the 15-fold faster dissolution rate of unoxidized ATM-106 fuel particles, compared to grains (Figure 1), should correlate with three times the grain-boundary exposure of the ATM-105 fuel particles. That is, the outer six to nine layers of grain boundaries of the unoxidized ATM-106 fuel particle specimen were apparently exposed to water. Also by similar argument, the 30-fold faster dissolution rate of oxidized ATM-106 fuel particles, compared to grains (Figure 1), should correlate with a dozen or more layers of grain boundaries exposed to water. Ceramographic examination of the particles is planned to help determine whether that argument is correct.

Dissolution Rate of Tc from U_4O_9+x Spent Fuel

Figure 2b shows that Tc initially dissolved nearly ten times faster than U from oxidized ATM-105 fuel particles. This result led to the original speculation about the potential generality of enhanced Tc dissolution from oxidized fuels and the possible mechanisms involved, which are described in the introduction to this paper. However, Figure 1b shows Tc initially dissolved less than three times faster than U from oxidized ATM-106 fuel particles. This difference in Tc behavior for the two oxidized fuels also continued into the longer-term Tc dissolution results.

The Tc/U dissolution ratio, after a few days, was about one for the oxidized ATM-105 grains (Figure 2a), but only about 0.5 for the oxidized ATM-106 grains (Figure 1a). This suggests that a larger fraction of the Tc is contained in the hard-to-dissolve ϵ -phase metallic particles in the ATM-106 fuel. If that is true, it may also explain why there was a slower initial rate of Tc dissolution from the ATM-106 fuel. The fraction of Tc contained in the ϵ -phase particles is not well known from other analytical methods for either fuel. However, it is known that the size of the ϵ -phase particles is greatly increased near the center of ATM-106 fuel⁶. Perhaps the smaller surface-to-volume ratio of the larger ϵ -phase particles in the ATM-106 fuel specimens can account for the slower Tc dissolution rates.

Dissolution of Cs and U from ATM-106 Spent Fuel Oxidized to U_3O_8

A major reason for conducting dissolution tests with spent fuel oxidized to U_3O_8 was to determine whether the inter- and intra-granular cracks produced by the oxidation would lead to high initial dissolution rates of soluble radionuclides, as was postulated in the introduction to this paper. Therefore, 100% of the test-column effluent was collected and analyzed for each of the first two days. During the first day (29 h), 16.2% of the total Cs inventory dissolved compared with 4.5% of the U; thus the excess of Cs over U was about 12%, which represents the amount exposed by oxidation-induced cracking and grain-boundary opening. Nearly congruent dissolution of Cs and U was observed during the second and subsequent days. This confirms the postulate that oxidation to U_3O_8 might expose a relatively large fraction of the Cs inventory to water where it could be readily dissolved, at least for this one type of spent fuel (ATM-106).

Figure 3 shows that the U dissolution rate of ATM-106 fuel oxidized to U_3O_8 stabilized at $\sim 15 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ after about 10 days. This is about 10 times faster than unoxidized ATM-106 grains and about twice as fast as grains oxidized to U_4O_9+x (Figure 1a). A more important effect of oxidation to U_3O_8 was the very large increase in surface area compared to the particles used to prepare the U_3O_8 (Table II). This resulted in a fractional dissolution rate (rate per unit sample weight of uranium) of U_3O_8 equal to 150 times that of the unoxidized particles.

Dissolution of Tc from ATM-106 Spent Fuel Oxidized to U_3O_8

An unexpected result of oxidizing ATM-106 fuel to U_3O_8 was the slow dissolution of Tc. Initially the Tc dissolved even slower than U, rather than faster as was expected. After the first few days, the Tc/U dissolution ratio was only 0.1 to 0.2. This was substantially less than the Tc/U dissolution ratio of about 0.5 that was observed and discussed above for ATM-106 grains oxidized to U_4O_{9+x} . It was first thought that the higher temperatures needed to generate U_3O_8 during the short-time laboratory exposure may have vaporized a large fraction of the Tc, perhaps as the volatile compound Tc_2O_7 .⁷ However, measurement of the total Tc remaining in the U_3O_8 indicated that little or no Tc had been lost. Thus, the reason for the low Tc dissolution rate remains unresolved.

Mechanistic Implications

Although the difference in intrinsic dissolution rates between oxidized and unoxidized ATM-106 fuel specimens was larger than for ATM-105 fuel or unirradiated UO_2 ,¹ it was still a factor of 10, or less, even for fuel oxidized to U_3O_8 . This difference seems relatively small when it is considered that the surface of UO_2 must first oxidize to a stoichiometry equivalent to approximately $UO_{2.33}$ before soluble U(VI) species can leave the solid surface and enter the solution.⁸ These observations lend support to our previous contention¹ that initial surface oxidation is not involved in a rate-limiting step of the UO_2 oxidation/dissolution mechanism.

CONCLUSIONS

This paper reports results from the first portion of a dissolution testing program involving spent fuels that were previously air-oxidized to different higher oxidation states. The following conclusions can be drawn from these initial results.

Air oxidation of spent fuel to U_4O_{9+x} had little effect on the U dissolution rate of a moderate-burnup, low fission-gas-release fuel but a more pronounced effect on a higher-burnup, high fission-gas-release fuel.

The initial dissolution rate of Tc from spent fuel oxidized to U_4O_{9+x} may correlate with fission gas release or another fuel parameter that is not yet defined. However, the results are complicated by the tendency of Tc to reside, at least partially, in ϵ -phase metallic particles that are relatively insoluble.

The very low Tc dissolution rate measured for spent fuel oxidized to U_3O_8 is not understood. This further complicates the interpretation of Tc dissolution rates from oxidized spent fuels.

As expected, rapid dissolution of a significant fraction of the total Cs inventory was observed for the one type of spent fuel that was oxidized to U_3O_8 .

Based upon the initial results of this testing program, it is evident that additional fuels must be tested to clarify the effect that air oxidation of the fuel has on the dissolution rates of the different radionuclides.

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Figure 1. Dissolution Rate of ATM-106 Spent Fuel in $2 \times 10^{-2} \text{ M NaHCO}_3$, 0.2 atm O_2 , $\text{pH} = 8$, 25°C .

Figure 2. Dissolution Rate of ATM-105 Spent Fuel in $2 \times 10^{-3} \text{ M NaHCO}_3/\text{Na}_2\text{CO}_3$, 0.2 atm O₂, pH = 9, 50°C.

Figure 3. Dissolution Rate of Oxidized ATM-106 Spent Fuel (U_3O_8) in $2 \times 10^{-2} M$ $NaHCO_3$, 0.2 atm O_2 , pH = 8, 25°C.

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