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UO_2 MATRIX DISSOLUTION RATES AND GRAIN BOUNDARY INVENTORIES OF Cs, Sr, and Tc IN SPENT LWR FUEL

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ABSTRACT

Experimental methods have been developed for measuring the grain-boundary inventories of radionuclides and for determining whether the UO_2 matrix of spent light-water reactor fuel dissolves congruently. Both methods depend upon first separating the fuel into individual grains. With the grain boundaries thus exposed, the associated inventories of radionuclides can be completely dissolved and measured. To determine whether the UO_2 matrix of spent fuel dissolves congruently, the fuel grains were placed in a flow-through column and water was pumped through the column at a rate sufficient to maintain the concentration of U in the column effluent far below saturation. Once the grain-boundary material has dissolved, the forward dissolution rate of the UO_2 matrix can be measured and, by measuring the concentrations of other radionuclides in the column effluent, the degree of congruency of the dissolution process can be determined. Data obtained to date indicate that the grain-boundary inventories of Cs, Tc, and Sr are approximately equal to gap inventories and that the fractional dissolution rate of Cs from the UO_2 matrix is approximately equal to that of U, i.e., the Cs and U dissolved nearly congruently. In addition, the data appear to show a gradient in the concentrations of Cs and Sr across the individual UO_2 grains.

INTRODUCTION

Calculations of the release of radionuclides from a geologic repository must treat soluble and insoluble radionuclides differently. Tests have shown that the actinide elements are so insoluble under most potential repository conditions that their release will be limited by the solubilities of the actinide-bearing solids and the flow rate of water through the waste package.[1] Actinide release is unlikely to be affected by the properties or behavior of the waste form itself. On the other hand, the release of highly soluble radionuclides of interest (e.g., ^{135}Cs, ^{99}Tc, and ^{129}I) will be partially dependent on the properties of the waste form.

Considerations of spent fuel as a waste form must take into account the heterogeneity of the fuel. It is generally agreed that the dissolution of soluble radionuclides from spent fuel can be divided into components that originate from three regions: 1) the fuel/cladding gap, which includes the spaces between fuel pellets and the open porosity and cracks within the pellets; 2) the grain boundaries of the fuel pellets; and 3) the UO_2 matrix.[2-4] The dissolution and release of radionuclides from these three regions of the fuel takes place at progressively decreasing rates. The first two occur relatively rapidly because the soluble radionuclides in the gap and grain boundaries are relatively accessible by water. The long-term dissolution rate of soluble radionuclides is much slower and is expected to be dominated by the rate of oxidation and congruent dissolution of the UO_2 fuel matrix.

In currently accepted models[2-4], spent fuel dissolution is treated as the sum of three independent terms corresponding to the three regions identified above. The problem in evaluating spent fuel as a waste form is

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that conventional tests on unclad but intact spent fuel fragments result in simultaneous but unequal rates of dissolution of radionuclides from all three of the regions. In these tests, there is no way to evaluate how much of a radionuclide came from each region, and apparent incongruent dissolution is almost always observed. To circumvent this problem and to understand the long-term dissolution behavior of spent fuel, the three regions must be tested separately.

The inventories of radionuclides within the gap can be measured using short-term dissolution experiments. These types of experiments have been used by a number of researchers for several years. For Canadian CANDU fuels, the gap inventories of Cs and I have been successfully correlated with release of the fission gases, which, in turn, have been correlated with the burnup and power history of the fuel.[5,6] However, because of the difficulty of separating spent fuel into its different components for individual testing, few previous attempts have been made to obtain unequivocal measurements of grain-boundary inventories or to test the dissolution behavior of spent fuel grains without the complicating effects of the simultaneous dissolution of radionuclides from the gap and grain boundaries. In this paper, methods are described for 1) measuring the inventory of radionuclides within the grain-boundary regions, and 2) measuring the dissolution rate of the UO_2 matrix and determining whether it dissolves congruently.

EXPERIMENTAL

Relevant parameters of the spent fuel samples tested in this work are given in Table I along with references in which the characterization of the fuel is reported.

TABLE I. Spent fuel characteristics

Fuel	Type	Burnup (MWd/kgM)	Fission Gas Release (%)	Reference
Turkey Point	PWR	28	0.1 to 0.3	[7]
ATM-103	PWR	30	0.25	[8]
ATM-105	BWR	28	0.59	[9]
ATM-106	PWR	43	7.4	[10]

The method used in this study for measuring grain-boundary inventories involved limited oxidation of spent fuel in air at low temperatures (150°C to 200°C), which resulted in preferential oxidation along the grain boundaries. Figure 1 shows a band of oxidized material surrounding most of the grains in a fuel sample where the average oxygen-to-metal ratio (O/M) = 2.159 based on weight-gain measurements. The fraction of the fuel that was oxidized can be calculated from the weight-gain measurements because the oxidized regions are known to be nearly stoichiometric U_4O_9.[11] Oxidation weakened the grain boundaries to the point where light crushing caused the fuel to separate into individual grains (Figure 2) thereby exposing essentially all of the grain boundaries. Following separation of the fuel into individual grains, those radionuclides positioned within or near the exposed grain boundaries were completely dissolved in 0.1 M HCl during short-term (3-hour) dissolution tests in which the acid was changed and analyzed frequently. The fraction of U dissolved from the samples in these tests can be subtracted from the fractions of the other radionuclides dissolved, and the difference can be attributed to the portion of the different radionuclides that reside in excess at or near the surface of the exposed grain boundaries.

A slightly different method was used to prepare individual grains and subgrains of spent fuel for the matrix dissolution measurements. Earlier work had shown that dissolution of the oxidized portions surrounding the fuel

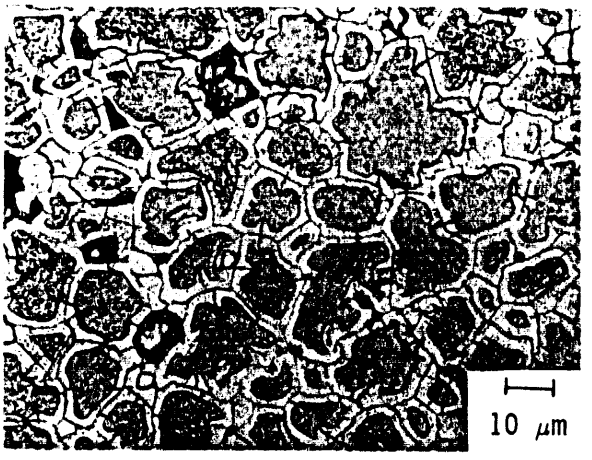

Fig. 1. ATM-103 fuel particle oxidized in air at 195°C for 335 hours

Fig. 2. Same fuel shown in Fig. 1 after crushing to separate fuel into individual grains

grains prepared as described above (as was originally intended) was difficult or impossible to do in a controlled manner. Therefore, fuel for the matrix dissolution measurements was simply pulverized and screened (using screens with openings of 20 μm to 32 μm, as appropriate) to eliminate virtually all of the multigrain particles resulting in a specimen composed primarily of individual grains. Since unoxidized fuel also fractures preferentially along grain boundaries, this technique was used to expose almost all of the grain boundaries, but it produced somewhat more transgranular fracturing than occurred with the partially oxidized fuel as shown in Figure 3. However, transgranular fracture surfaces were of no consequence for matrix dissolution tests; it was only important to expose all of the grain boundaries so that they could be completely dissolved to leave clean fuel grains for subsequent testing.

Originally, the fuel grains prepared by pulverizing the fuel were placed in 0.1 M HCl for 60 minutes to dissolve the exposed grain-boundary material prior to placing them in the flow-through columns for the dissolution-rate measurements. Later it was determined that as-prepared fuel grains could be placed directly in the columns because the grain-boundary material was removed during the first few days in the columns, and subsequent data were applicable to "clean" fuel grains.

The columns, which were made of stainless steel, used in the flow-through tests were 50 mm long X 6.35 mm inside diameter. Stainless steel frits with 2-μm openings were placed on both ends. The best combination of sample size and flow rate was found to be 50 to 150 mg (i.e., the fuel sample occupied only a small fraction of the volume in the column) and 0.1 to 1.0 mL/min, respectively. Under these conditions, the concentrations of U in the column effluents remained far below saturation where U dissolution rates were found to be independent of flow rate (i.e., U concentrations were demonstrated to be proportional to the reciprocal of the flow rate). This allowed the forward dissolution rate of the UO_2 matrix to be measured and, by measuring the

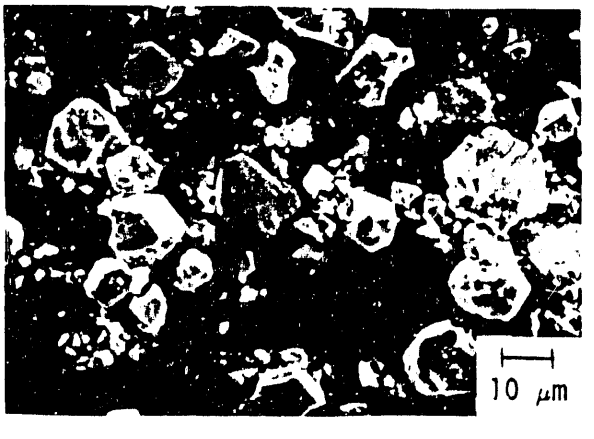

Fig. 3. ATM-103 fuel crushed without prior oxidation

concentrations of other radionuclides in the column effluents, the degree of congruency of the dissolution process to be determined.

RESULTS

Figures 4 and 5 show the results of short-term dissolution tests intended to reveal the fraction of certain radionuclides that were concentrated at or near the grain boundaries as determined by subtracting the fraction of U dissolved from the fractions of each of the other radionuclides dissolved. Data in Figure 4 indicate differences between Cs and U of about 0.35% independent of the degree of oxidation. However, differences between Tc and U were no more than about 0.1% for the lightly oxidized fuel but were 0.15% to 0.25% for the highly oxidized fuel. This apparent dependence of excess Tc dissolution on fuel oxidation was further explored by subsequent tests, the results of which are shown in Figure 5. Again, the difference between Tc and U was greater for the oxidized fuel. In addition, the data in Figure 5, unlike those in Figure 4, indicate that the difference between Cs and U is smaller for the oxidized fuel.

It should be pointed out that the more highly oxidized samples in both Figures 4 and 5 are believed to have smaller surface areas than the lightly oxidized or unoxidized samples. Therefore, the larger percentage of U that dissolved from the more oxidized samples cannot be unequivocally attributed to the oxidization itself. However, the important features of these data, which are the differences between U and the other elements, are not expected to be affected by the relative surface areas.

One difference between the tests represented by the data in Figures 4 and 5 is that the ATM-103 fuel (Figure 5) was placed in deionized water (DIW) at ambient temperature for 1 week to dissolve gap-inventory material immediately following discharge from the cladding. This "clean" fuel was then used to prepare fuel samples for subsequent grain-boundary inventory measurements. Removal of the gap inventory was not done with the Turkey Point (TP) fuel in Figure 4. Thus, differences in fractional dissolution between U and the other radionuclides in Figure 4 may include a portion of the gap inventories as well as the grain-boundary inventories. These differences in Figure 5 should not include any gap-inventory material.

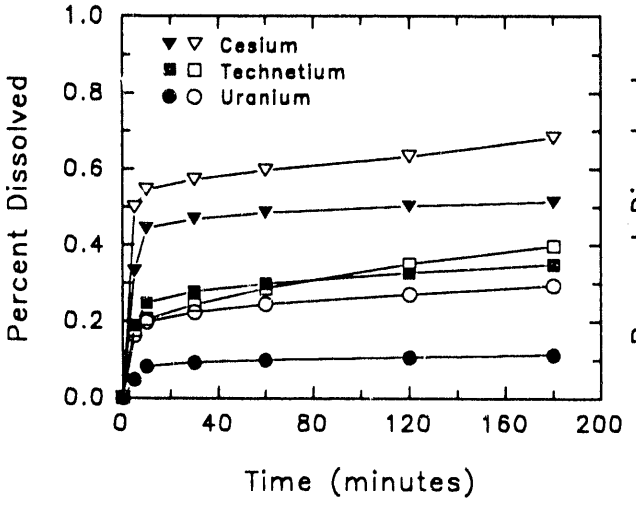

Fig. 4. Cumulative fraction of radionuclides dissolved from TP fuel in 0.1 M HCl. Closed symbols for fuel oxidized to 6% U_4O_9; open symbols 65% U_4O_9.

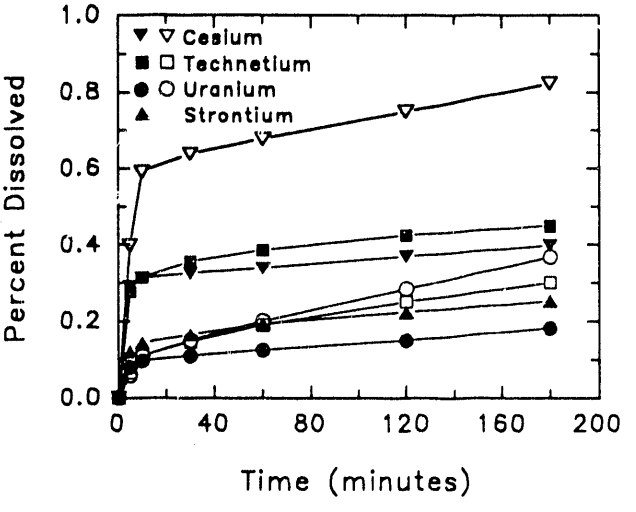

Fig. 5. Cumulative fraction of radionuclides dissolved from ATM-103 fuel in 0.1 M HCl. Closed symbols unoxidized fuel; open symbols for fuel oxidized to 63% U_4O_9.

Figure 6 shows inventory-normalized[a] Cs/U ratios obtained during 330 days of flow-through tests with ATM-105 fuel in DIW. Because the ratios remained slightly above the congruent value of 1.0 and because it was discovered that some of the particles in the sample of fuel being tested were multigrain rather than individual grains as intended, a second sample was prepared and tested. Multigrain particles were eliminated from the second sample by passing the crushed fuel particles through a screen with 20-μm openings. These fuel grains were placed in two columns, one with DIW and the other with 0.01 M HCl. The dilute acid was expected to increase the dissolution rate but not affect the Cs/U dissolution ratio and was chosen to allow that ratio to be followed through dissolution of the entire sample in a shorter period to time.

Figure 7 shows inventory-normalized Cs/U dissolution ratios for the newly prepared ATM-105 fuel samples in DIW and 0.01 M HCl; the reason for the switch to HCl in Figure 7 is described below. Data in the DIW portion of Figure 7 (first 141 days) match those in Figure 6 quite well indicating that the slightly elevated Cs/U ratio was not caused by multigrain particles as first thought. Data in Figure 8, which cover the dissolution of almost the entire sample over a period of 116 days, show that the Cs/U ratio (and the Sr/U ratio as well) remained above 1.0 until after about 75% of the sample had dissolved, after which the ratio dropped to values less than 1.0 as it must to maintain a strict mass balance.

Because of the rather abrupt drop in the Cs/U ratio after about 75% of the sample had dissolved (Figure 8), a decision was made to change the water in the other column (Figure 7) to 0.01 M HCl to determine if the abrupt drop could be reproduced. Following the change in solvent, the Cs/U ratio was observed to decrease below the congruent value of 1.0 after about 50% of the sample had dissolved, but the abrupt drop was not reproduced. The fact that the results in both Figures 7 and 8 show a trend in the Cs/U ratio from greater than 1.0 to less than 1.0 provides an indication of a Cs concentration gradient across the fuel grains.

The inventory-normalized Sr/U ratios in Figure 8 follow the Cs/U ratios quite well. However, the Tc/U ratios fall well below 1.0 throughout dissolution of essentially the entire sample. The Tc analytical procedures

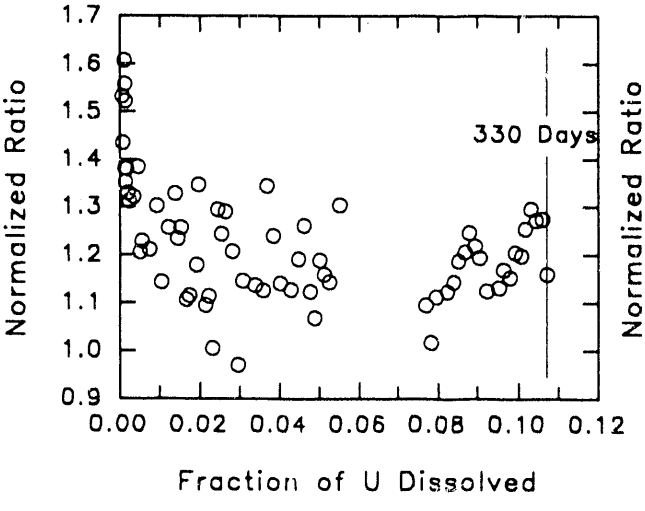

Fig. 6. Cs/U normalized dissolution ratio for ATM-105 fuel in DIW

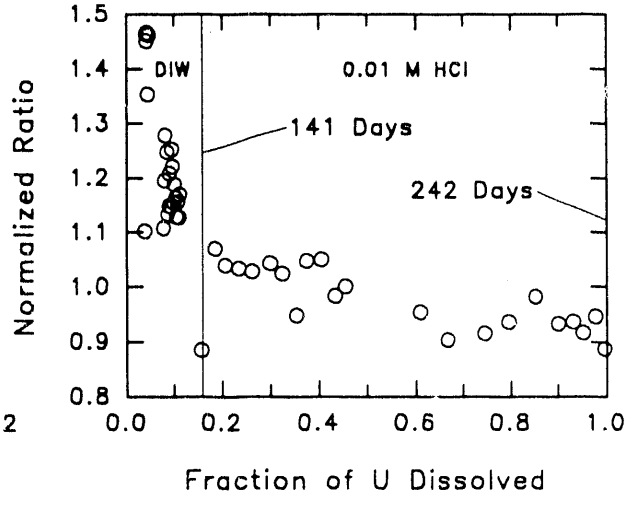

Fig. 7. Cs/U normalized dissolution ratio for ATM-105 fuel in DIW and 0.01 M HCl

(a) Inventory normalization takes into account the amount (inventory) of each element originally present in the spent fuel sample. Thus, for example, the Cs/U normalized ratios represent the fraction of Cs dissolved divided by the fraction of U dissolved.

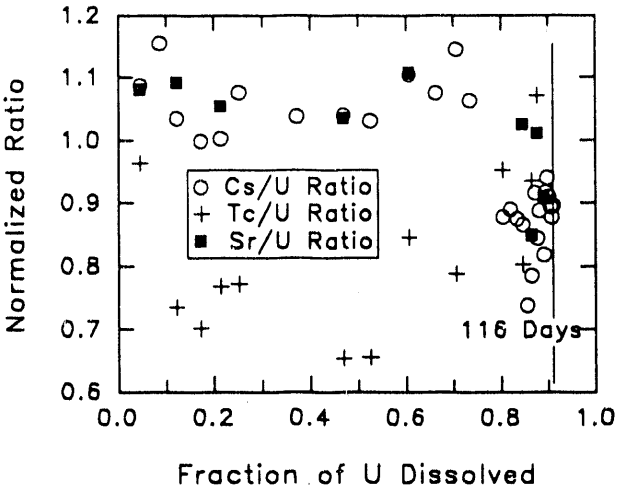

Fig. 8. Normalized dissolution ratios for ATM-105 fuel in 0.01 M HCl

and data were carefully reexamined, and some additional samples were analyzed for Tc. The original Tc data appear to be reliable, and the newer data were in agreement; both are plotted in Figure 8. A possible explanation is that some of the Tc resides in the ϵ-ruthenium phase that has been observed in spent fuel[12] and is, therefore, in a form that does not dissolve in these tests.

Figures 9 and 10 show inventory-normalized Cs/U dissolution ratios in DIW and 0.01 M HCl respectively for ATM-106 fuel samples that were crushed and passed through a screen with 32-μm openings. Again, the Cs/U ratios remained above 1.0 until a relatively large fraction of the fuel had dissolved; it then dropped below 1.0, consistent with good mass balance. Agreement between the DIW and HCl data is reasonably good; the first data point in Figure 10 occurs at a fraction-of-U-dissolved value of 0.024, and the Cs/U ratio at that point is approximately equal to the Cs/U values for the same fraction of dissolved U shown in Figure 9. Thus, these data provide evidence for a Cs concentration gradient across the grains of this fuel also. Figure 11 shows U dissolution rates of ATM-105 and ATM-106 fuels in DIW. The data were normalized on the basis of surface areas that were estimated from measurements of particle size distributions, which were grouped into particle-size increments 0.5 μm in width. Specific surface areas, assuming spherical particles, were calculated for each of these increments and multiplied by the fraction of particles within each increment. Summing these data over the entire size range resulted in specific surface areas for the samples as a whole, based on the assumption of spherical particles. These calculated values were doubled[a] to account

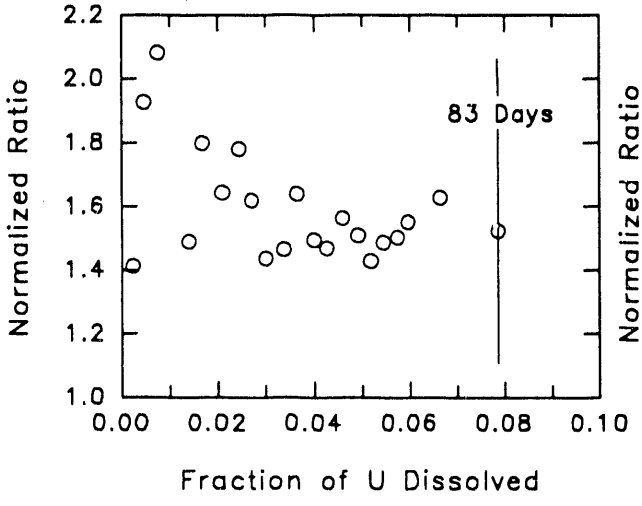

Fig. 9. Cs/U normalized dissolution ratio for ATM-106 fuel in DIW

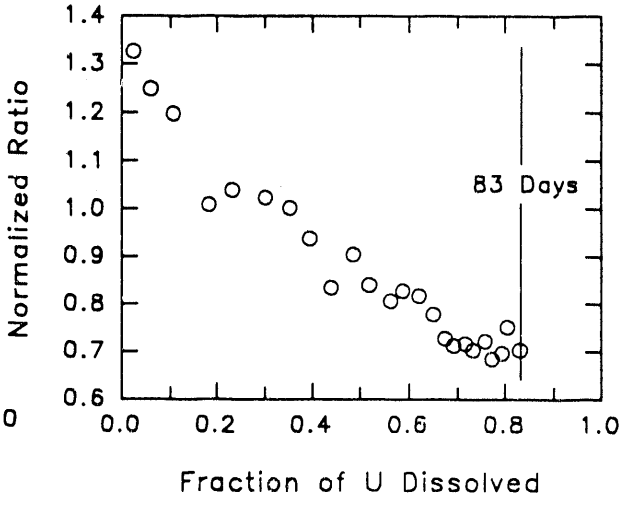

Fig. 10. Cs/U normalized dissolution ratio for ATM-106 fuel in 0.01 M HCl

(a) A surface roughness factor of 2 is an estimate based on observation of the particles with scanning electron microscopy (SEM). Surface roughness factors anywhere between 1 and 5 could be equally valid.

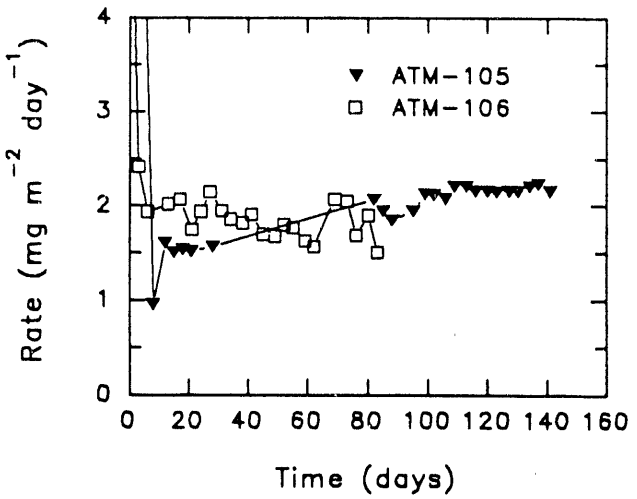

Fig. 11. Normalized U dissolution rates in DIW

for the fact that the particles were irregular rather than spherical in shape.

The data in Figure 11 can be compared with dissolution rates measured for unirradiated UO_2 powder earlier in this program of 0.13 mg/m^2•day based on sample surface area measured by the BET method or 0.24 mg/m^2•day based on sample surface area estimated from the measured particle size distribution in the same manner described above for the spent fuel. An exception to the latter method was that a surface roughness factor of 5 was applied to the unirradiated UO_2 because SEM images showed a much rougher surface than was the case with the spent fuel particles. In a review by Johnson and Shoesmith[13], UO_2 dissolution rates under the conditions used in the present tests are depicted to range upward by a factor of perhaps 10 from about 0.8 mg/m^2•day. This range includes the values obtained in this study for spent fuel but is a little higher than the values obtained for unirradiated UO_2.

CONCLUSIONS

Partial oxidation of spent fuel in air at low temperatures was shown to be an effective first step in the preparation of individual fuel grains with a minimum of transgranular fracturing. However, oxidation also changed the results of the grain-boundary-inventory measurements in a way that cannot yet be rationalized. Since satisfactory grain-boundary-inventory measurements can apparently be achieved using fuel grains prepared without partial oxidation of the fuel, the oxidation step probably should be avoided in future tests.

The grain-boundary inventories of Cs were measured for two different low fission-gas-release fuels. In both cases, the fraction of Cs that could be attributed to the grain-boundary inventory was roughly equal to the fission-gas-release values (0.2% to 0.4% of the Cs compared to 0.1% to 0.3% of the fission-gas release). The grain-boundary inventories of Tc and Sr were smaller than those for Cs in the one fuel tested. Grain-boundary inventory measurements need to be extended to fuels with high fission-gas-release to determine whether there is a good correlation between the two parameters as expected.[a]

Inventory-normalized Cs/U dissolution ratios were measured for the UO_2 matrices of both a low fission-gas-release fuel and a high fission-gas-release fuel. The ratios in both cases were in the range 1.0 to 1.4 (nearly equal to the congruent ratio of 1.0) until large fractions of the fuels had dissolved, after which the ratios decreased to less than 1.0. These data suggest that Cs concentration gradients exist across the fuel grains giving

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(a) A good correlation between fission-gas release and fuel/cladding gap inventories of Cs and I has been demonstrated for Canadian CANDU fuels.[5, 6] A correlation between fission-gas release and grain-boundary inventories for CANDU fuels is also expected on the basis of computer modeling efforts.[13] Similar correlations are generally expected for U.S. light-water-reactor fuels, but experimental evidence to support such expectations is meager.

rise to the slightly elevated Cs/U dissolution ratio during the first part of the tests. Similar results were obtained for Sr in the low fission-gas-release fuel (the only fuel tested for which Sr data have been collected). The Tc/U ratios appear to indicate that some of the Tc is in an insoluble form such as the ε-ruthenium phase that has been observed in spent fuel.[12] However, further testing is required before these results can be generally accepted.

Dissolution rates in DIW were also measured for both the low and high fission-gas-release fuels. The results for the two fuels were indistinguishable but were about 10 times higher than measured for unirradiated UO_2. The dissolution rate of unirradiated UO_2 measured in the present study is lower by perhaps a factor of 4 compared with values published by several other researchers as reviewed by Johnson and Shoesmith.[13] However, comparison of data from different studies is limited by the uncertainties in the present data arising from surface area measurements in which the particles were assumed to be spherical with surface roughness factors between 1 and 5.

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