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by

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ABSTRACT

Dissolution rates have been measured for spent fuel in both unoxidized and partially air-oxidized conditions (oxygen-to-metal ratio of 2.4 with U_4O_9 crystallographic structure), as well as for unirradiated UO_2 and UO_2 that was partially oxidized to U_3O_7. All measurements were taken in flow-through tests where uranium concentrations were maintained well below solubility limits to avoid suppression of the measured dissolution rates by solubility constraints. No significant differences in dissolution behavior were found between the oxidized and unoxidized spent fuel or between unirradiated UO_2 and U_3O_7.

INTRODUCTION

Spent fuel is being evaluated as a waste form for disposal in a geologic repository. Dissolution and transport of radionuclides from the fuel as a result of contact with groundwater are generally accepted as the primary mechanisms by which the radionuclides could be released from a repository.[1] The potential repository site at Yucca Mountain Nevada is in the unsaturated zone; that is, the amount of groundwater is limited so the rocks and soil are not saturated with water, and atmospheric air has access to the zone. Should a waste container and the fuel cladding both fail in such a repository, the spent fuel may be contacted by air and be partially oxidized before it is contacted by water.

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Electrochemical studies performed with unirradiated UO_2 indicate that the dissolution mechanism is one in which the surface must first oxidize to a stoichiometry of approximately $UO_{2.33}$, or higher, prior to dissolution of uranium atoms in the +6 oxidation state from the surface.[2,3] Other studies[4] have shown that the dissolution rate of UO_2 has a first order dependence on dissolved oxygen concentration. These results indicate that oxidation is involved in a rate-limiting portion of the dissolution process. Because the presumed rate-limiting oxidation step has already occurred in air-oxidized specimens, it has been commonly assumed that pre-oxidized UO_2 (and spent fuel as well) will dissolve at a faster rate than unoxidized UO_2. However, this assumption has not been carefully tested, even with unirradiated UO_2. Also, U.S. light water reactor (LWR) spent fuel oxidizes differently from unirradiated UO_2, as described below, which could lead to differences in dissolution mechanisms.

Unirradiated UO_2 initially oxidizes in air at temperatures up to about 250°C by forming thin surface layers with a stoichiometry of approximately $UO_{2.33}$ and a crystal structure of tetragonal or lower symmetry based on the original UO_2 structure.[5,6] These phases are often simply identified as U_3O_7. Further oxidation of the unirradiated material produces friable U_3O_8 that usually degrades to powder. In contrast, oxidation studies with U.S. LWR spent fuel[7] indicate that at temperatures up to about 200°C in air, the fuel oxidizes rapidly along grain boundaries and forms cubic U_4O_9 with an oxygen-to-metal (O/M) ratio of 2.4 rather than the expected ratio of 2.25. The observed phase can be written as U_4O_{9+x}. In laboratory tests up to 195°C, the spent fuel oxidation effectively ceased at the O/M ratio of 2.4 and the U_4O_9 crystal structure, and formed no detectable higher oxides in thousands of

hours at temperature.[7] Given enough time at temperatures below 200°C, spent fuel may oxidize past the $UO_{2.4}$ stage, but the requisite time/temperature relationship is not presently known.

To test the assumption that pre-oxidized fuel will dissolve faster than unoxidized fuel, dissolution tests were performed with spent fuel oxidized to U_4O_{9+x}. More highly oxidized fuel should also be tested because of the possibility that U_4O_{9+x} may not be the highest oxidation state that could eventually develop under repository conditions. However, the next oxidation state has not been determined. Because U_3O_7 may eventually develop in some types of spent fuel, tests were conducted using unirradiated U_3O_7 as a stand-in for the fuel, which is not presently available in U_3O_7 form. Also, dissolution rate tests with unirradiated U_3O_7 would be useful for comparison with the ongoing Canadian electrochemical studies.[2]

This paper reports results of four dissolution rate tests with partially oxidized spent fuel and unirradiated UO_2. Spent fuel oxidized to nearly 100% U_4O_{9+x} was tested along with unoxidized specimens of the same fuel. Results are also reported for unirradiated UO_2 and U_3O_7.

EXPERIMENTAL

A method has been developed for removing the soluble radionuclides concentrated within the fuel/cladding gap and grain boundaries of spent fuel during the preparation of specimens for dissolution testing.[8] The dissolution rate of the UO_2 matrix of the fuel can thus be tested separately without any contribution from the gap and grain boundary regions. The method involves crushing the fuel, which fractures preferentially along the grain boundaries, and passing the crushed fuel through screens with small openings (20 to 32 μm) to remove multigrain particles (grain sizes of the fuels tested have ranged

from 15 to 25 μm). Small subgrain particles are removed by washing the screened fuel grains in dilute carbonate solution with the aid of vigorous stirring and ultrasonic agitation. The fine particles then separate from the larger particles and remain suspended in solution as the larger particles settle to the bottom. The small particles remain in suspension long enough to be decanted along with the solution. A few repetitions of this washing procedure, followed by washing with deionized water to remove the carbonate, produce clean fuel grains with few, if any, small subgrain particles remaining, as shown in Figure 1. Also, because the crushing and screening process exposes virtually all of the grain boundaries to the solution, the soluble gap and grain boundary elements are also dissolved by the washing procedure. Dissolution rates of the clean spent fuel grain specimens are then measured in a dynamic flow-through system[9] where U concentrations are kept well below the solubility limit so that true forward kinetic rate constants can be determined.

Specimens of ATM-105 BWR spent fuel,[a] which were oxidized to the U_4O_{9+x} state in long-term tests at 175°C,[7] were prepared along with unoxidized specimens of the same fuel. Both materials were crushed, screened, and washed as described above to prepare clean fuel grains for dissolution testing (Figure 1 shows a portion of the oxidized fuel specimen). In addition, the wash solutions were analyzed to determine the amounts of U, ^{137}Cs, ^{99}Tc, and ^{90}Sr that dissolved during the washing process. Flow-through tests with both specimens were conducted in 2×10^{-3} M $Na_2CO_3/NaHCO_3$ solution, pH = 9.0 to 9.2,

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[a] Boiling water reactor spent fuel discharged in 1982 from the Cooper Nuclear Power Plant.[10] The specimens used in this work were from Rod ADD2974, which had a peak burnup of 31 MWd/kgM and a fission gas release of 0.6%.

at 50°C. This particular set of test conditions was chosen because the same conditions have been used for testing other spent fuel specimens at PNL and it will thus be possible to compare results.

Specimens of unirradiated UO_2 and U_3O_7 were prepared by first crushing UO_2 pellets and screening (-140/+325 mesh U.S. Standard Series) to produce particles in the nominal size range of 44 to 105 μm. These particles were then washed as described for the fuel grains to eliminate the very fine powder that adhered to the coarser particles. A portion of these clean particles was then oxidized in air at 225°C for 94 h, resulting in an average O/M ratio of 2.047 as determined by weight-gain measurements. X-ray diffraction (XRD) measurements of the as-prepared particles indicated the presence of a U_3O_7 surface layer and no detectable U_3O_8. In this case, a low-symmetry U_3O_7 variant similar to δ-U_3O_7 (U_8O_{19})[6] was produced instead of the more common β-U_3O_7. A scanning electron micrograph in Figure 2 shows the U_3O_7 phase around the periphery of the particles and indicates that the thickness of the oxidized layer is ~1 μm. For dissolution rate tests, oxidizing the particle surface to U_3O_7 is just as good as oxidizing the entire particle, since the test solution contacts only (or least predominantly) the outside surface of the particle. Flow-through tests with both the UO_2 and U_3O_7 particles were conducted in 2×10^{-2} M $NaHCO_3$ solution, pH = 8.0 to 8.2, at ambient temperature (~25°C).

To compare dissolution rate measurements for different test specimens, the data must be normalized on the basis of the surface area of the specimens. As there was no capability for measuring the surface areas of spent fuel specimens using the BET method, a method of estimating the specific surface areas of fuel grain specimens based on particle-size distribution measurements

was used instead. Specific surface areas were calculated from the particle-size distribution measured by a Brinkman particle size analyzer assuming that the particles were spherical in shape. Specific surface areas of the oxidized and unoxidized spent fuel specimens used in this study were calculated to be 304 cm^2/g and 328 cm^2/g, respectively. These values were multiplied by the same "surface roughness factor" of three found for the UO_2 powder described below. The resulting estimates, 912 cm^2/g and 984 cm^2/g, were used to normalize the data presented in Figure 3. Although these estimates may not be absolutely accurate, the relative errors for the two specimens would be about the same because of their similar morphologies and particle sizes. Therefore, comparison of dissolution rate data from the two specimens should be strictly valid even though the absolute values remain somewhat uncertain.

The specific surface area of the unirradiated UO_2 specimen used in this study was calculated from a particle-size distribution measurement to be 88.3 cm^2/g. A portion of the same batch of unirradiated UO_2 had a BET surface area of 267 cm^2/g as measured at Lawrence Livermore National Laboratory. This factor of three difference can be attributed to surface roughness. The specific surface area of the unirradiated U_3O_7 used in this study was assumed to be the same as the UO_2, 267 cm^2/g, because the light oxidation was expected to have a negligible effect on the surface area.

RESULTS

The screened and washed grains of unoxidized and partially oxidized spent fuel were placed in separate flow-through columns and tested with 2×10^{-3} M $Na_2CO_3/NaHCO_3$ solution, pH = 9.0 to 9.2, at 50°C. Figure 3 shows the resulting dissolution rates for the two specimens. The uranium dissolution rates that were normalized on the basis of surface area (left hand

scale in Figures 3 and 4) were nearly identical for the two specimens. This shows that pre-oxidation of spent fuel in air to the U_4O_{9+x} state does not lead to a higher uranium dissolution rate, as would have been expected on the basis of the argument presented in the introduction.

Using the right hand scale of Figure 3, the same fractional dissolution rates would be observed for all four elements if the fuel dissolved congruently. In fact, after the first few days, differences between the results for uranium and the other three elements were quite small. The slight excess of Cs compared to U was consistent with results reported earlier, where the slight excess was attributed to a Cs concentration gradient within the fuel grains.[8] The present Tc results were equal to or slightly above the U results; earlier data[8] showed a smaller fractional dissolution rate of Tc compared with U. The same fuel was involved in both the present and earlier tests. The discrepancy may have been due to the difference in test solutions (2×10^{-3} M $Na_2CO_3/NaHCO_3$ solution, pH = 9.0 to 9.2 in the present tests, 0.01 M HCl in the previous test). In any case, no significant difference was found in dissolution rates of the four elements between unoxidized and pre-oxidized spent fuel.

Figure 4 compares U dissolution rates for unirradiated UO_2 and U_3O_7. The latter were somewhat higher, but the difference was relatively small and simple variation from sample to sample cannot be entirely ruled out. Most importantly, the difference seems much smaller than expected based on the kind of argument presented in the introduction. Two things potentially could influence the results obtained with the U_3O_7 used in this study. One is that U_3O_8 below the detection limit of the XRD analysis could have formed on the surface. The other is that the surface area may have changed due to the

oxidation. In fact, the formation of U_3O_8 would, in itself, increase the surface area. This is because U_3O_8 has a much lower density than UO_2 or U_3O_7 and its formation could have caused cracking of the surface. However, because the dissolution rate measured for this specimen was essentially the same as for the UO_2 specimen, these are moot points; the oxidized material (no matter what its stoichiometry or surface area) was shown to dissolve no faster than UO_2. That is, if the U_3O_7 surface area were greater than assumed, then the true surface area normalized dissolution rate would be even lower than shown in Figure 4.

The solutions used to wash the fuel grains were analyzed to determine the effect of oxidation on the initial release of soluble radionuclides from gap and grain boundary regions. Table 1 lists the percentage of inventory of the various radionuclides that dissolved from the fuel specimens during the washing process. As expected, the ^{137}Cs values exceeded the U values because these wash solutions presumably dissolved a portion of the gap inventory[a] and all of the grain boundary inventory of ^{137}Cs from these specimens. The ^{90}Sr values were roughly the same as the U values, as expected, because a previous study has shown that gap and grain boundary inventories of ^{90}Sr are quite small.[11] Therefore, the fractions of ^{90}Sr that dissolved should be about equal to the fractions of U that dissolved. The ^{99}Tc results were inconsistent with those from a previous study,[11] which indicated that gap and grain boundary inventories of soluble ^{99}Tc are quite small. Based on that study, the fractions of ^{99}Tc that dissolved in the present tests were expected to be

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[a] A portion of the gap inventory of ^{137}Cs is located on cladding surfaces and exterior surfaces of the fuel pellets, neither of which were included in these tests. Therefore, only that portion of the gap inventory associated with open pores and crack surfaces was available to be dissolved.

TABLE 1. Dissolution of Spent Fuel During Washing

Element	% of Inventory Dissolved		Gap and Grain Boundary Contribution[a]	
	Oxidized Fuel	Unoxidized Fuel	Oxidized Fuel	Unoxidized Fuel
U	0.11	0.16	--	--
^{137}Cs	0.36	0.71	0.25	0.55
^{99}Tc	0.80	1.06	0.69	0.90
^{90}Sr	0.087	0.15	-0.02	-0.01

a These values were obtained by subtracting the U values in columns 2 and 3 from the values for each of the other radionuclides.

approximately equal to the fractions of U that dissolved, just as were the ^{90}Sr fractions. Again, the difference may be due to the difference in test solutions (carbonate solution at pH ~ 10 in the present case, 0.1 M HCl in the previous test).

Another feature of the data in Table 1 is the lack of any significant difference between the oxidized and unoxidized fuel specimens. The observed difference in the U results between the two specimens can be attributed to differences between the surface areas of the specimens or differences between the length of time the different specimens were exposed to the washing solutions. No attempt was made to keep either of these parameters the same for the two specimens. Therefore, only the differences between U and the other radionuclides can be legitimately compared between the oxidized and unoxidized specimens. Thus, the excess ^{137}Cs that originated within the gap and grain boundaries was 0.25% to 0.55% of inventory, which seems reasonable compared to the fission gas release for this fuel, which was 0.6%.[10] The excess ^{99}Tc was 0.69% to 0.90% of inventory, and the excess ^{90}Sr was essentially zero. The observed differences between the oxidized and

unoxidized fuel are thought likely to be random sample-to-sample variations and not the result of oxidation.

DISCUSSION

Data presented in this paper indicate that pre-oxidation in air had little or no effect on subsequent dissolution rates of unirradiated UO_2 or the spent fuel that was tested. Because dissolution rates have been reported to vary with dissolved oxygen concentrations, and because aqueous electrochemical studies indicate the need for oxidation to precede dissolution, the implication of these results seems to be that the nature of the oxidation in aqueous solution is somehow different from that of the oxidation that takes place in air. Some type of hydrated surface species may be involved in the oxidation/dissolution process in a way that is not altered by prior air-oxidation.

Data presented here show no significant difference in the dissolution of U, ^{137}Cs, ^{99}Tc, or ^{90}Sr between oxidized and unoxidized spent fuel specimens upon initial contact by water. However, two other studies conducted with partially oxidized spent fuel specimens indicated enhanced initial release of ^{99}Tc compared with unoxidized specimens. One study used fuel grain specimens, just like the present study, but the tests were conducted in dilute HCl solution rather than carbonate solution.[8] The other study was conducted with spent fuel fragments 2 to 5 mm in size, and the test solution was J-13 well water, which is a dilute bicarbonate-containing groundwater.[12] Because of the differences in the test specimens and test parameters among these three studies, the reason for the apparently conflicting ^{99}Tc results cannot be explained without further testing.

CONCLUSIONS

Air-oxidation of spent fuel to the U_4O_{9+x} state had no significant effect on subsequent steady-state dissolution rates of U, ^{137}Cs, ^{99}Tc, or ^{90}Sr measured in dilute carbonate solutions.

Air-oxidation of unirradiated UO_2 to form U_3O_7 had little or no significant effect on subsequent steady-state dissolution rates of U measured in dilute carbonate solutions.

The initial dissolution of ^{99}Tc (gap and grain boundary contribution) from both oxidized and unoxidized spent fuel specimens in carbonate solutions was greater than observed in previous measurements where the test solutions were either deionized water or dilute HCl solution.

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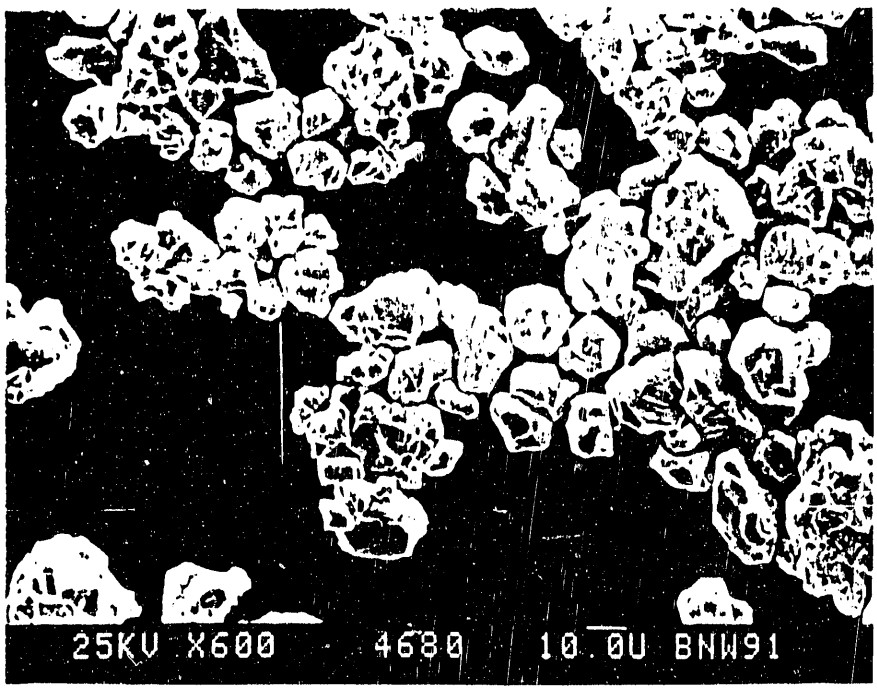

FIGURE 1. Scanning electron photograph of oxidized spent fuel grains after screening and washing.

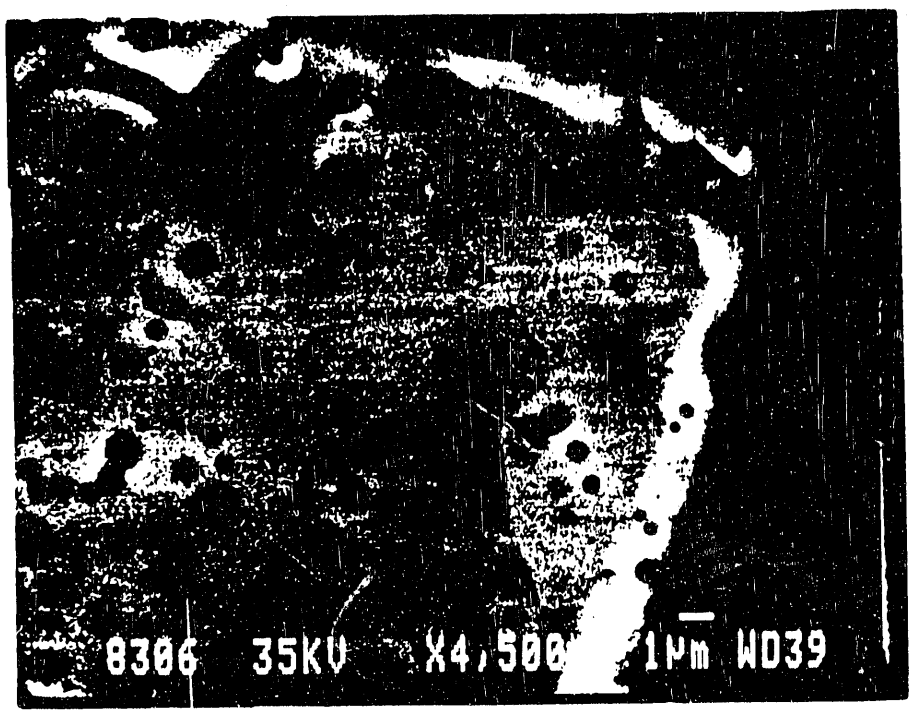

FIGURE 2. Scanning electron photograph of unirradiated UO_2/U_3O_7 particles.

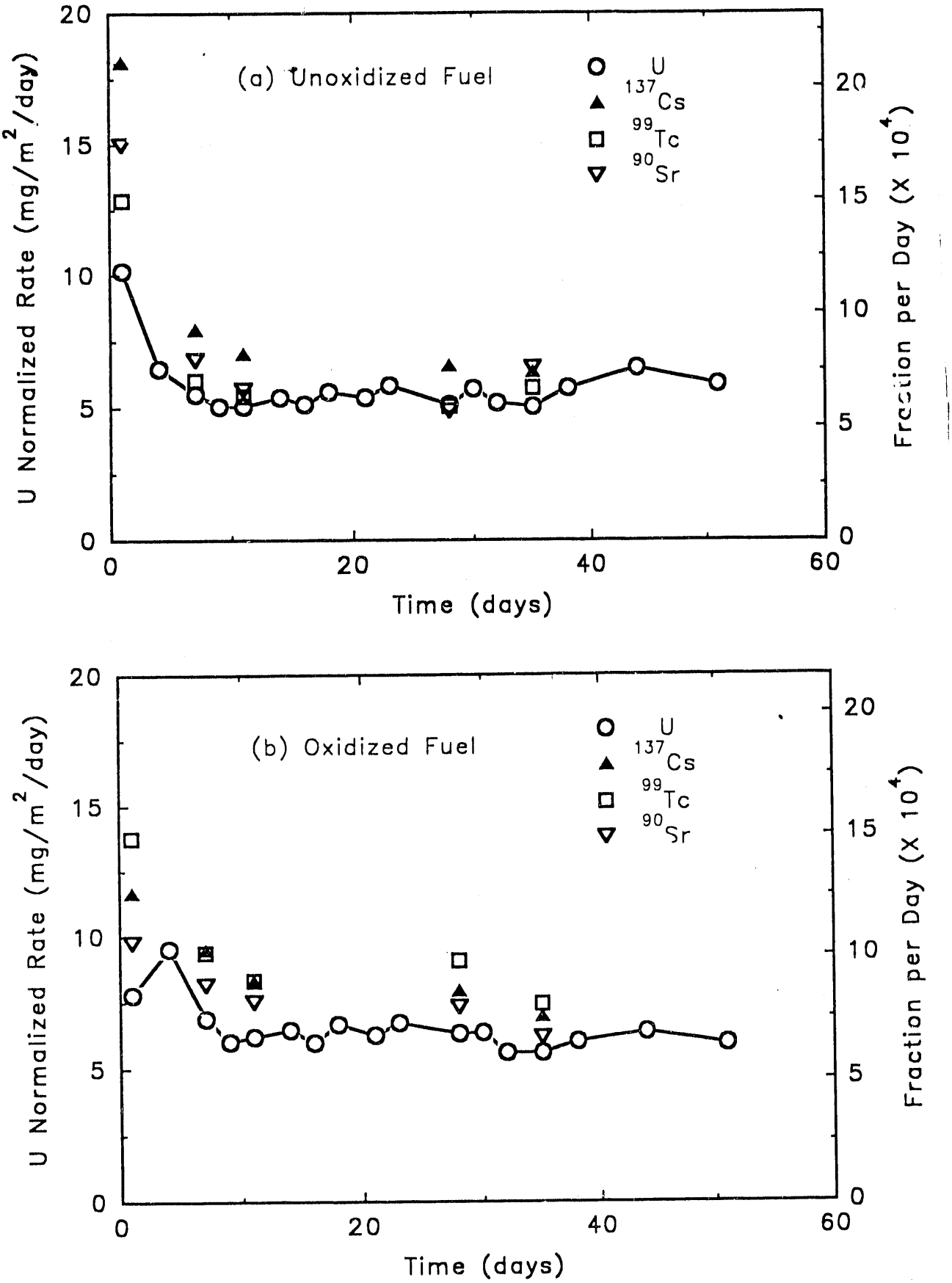

FIGURE 3. Dissolution rate of spent fuel in 2 x 10^{-3} M $Na_2CO_3/NaHCO_3$ solution, pH = 9.0 to 9.2, at 50°C. The left hand scale applies only to the uranium results, which were normalized on the basis of estimated surface areas. The right hand scale applies to all four elements and shows the fractional dissolution rate of each element based on the initial inventory of that element in the spent fuel.

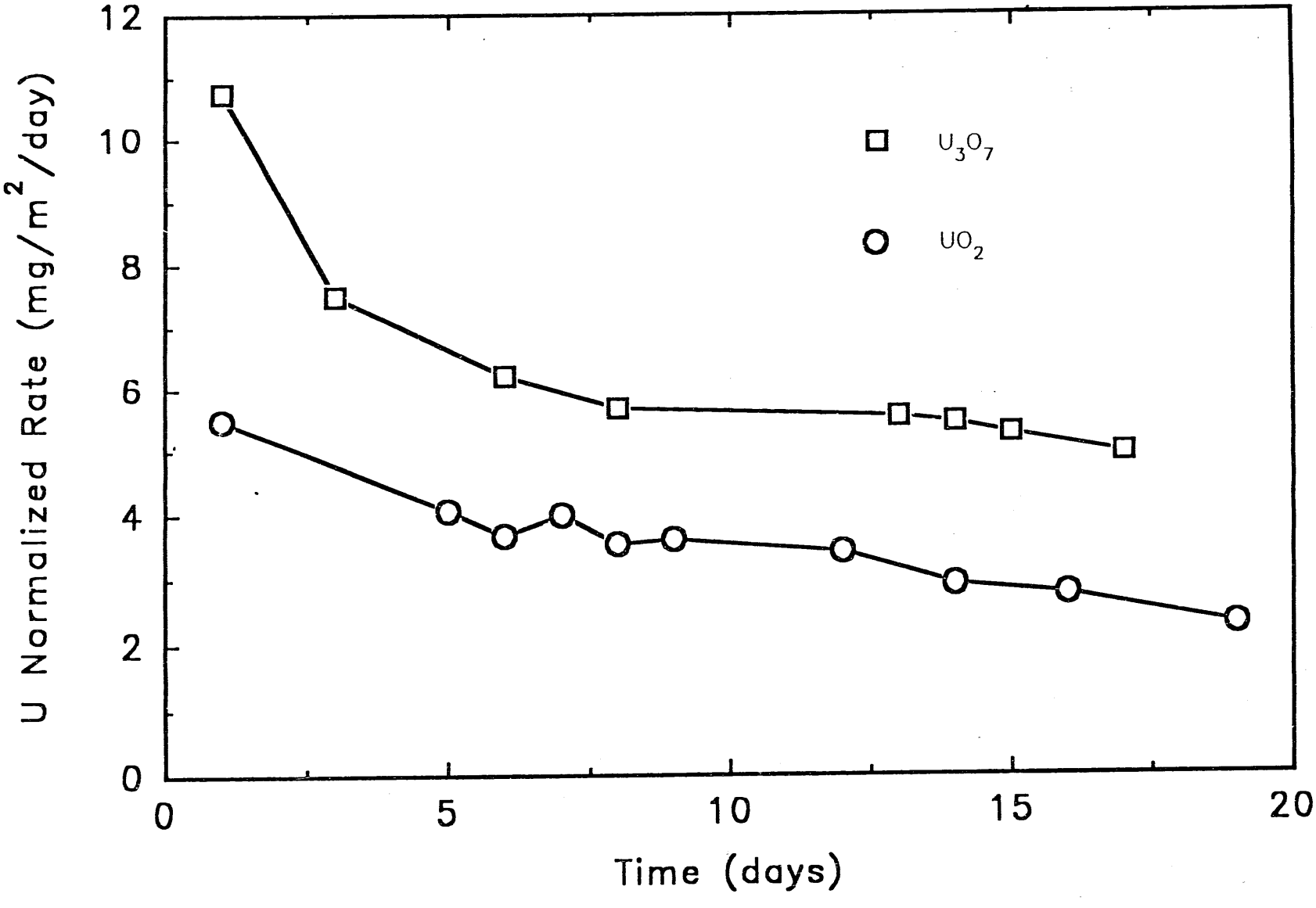

FIGURE 4. Dissolution rates of unirradiated UO_2 and U_3O_7 2×10^{-2} M $Na_2CO_3/NaHCO_3$ solution, pH = 8.0 to 8.2, at 25°C.

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