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**DISSOLUTION CHARACTERISTICS OF MIXED
UO₂ POWDERS IN J-13 WATER
UNDER SATURATED CONDITIONS**

by

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ABSTRACT

The Yucca Mountain Project/Spent Fuel program at Argonne National Laboratory is designed to determine radionuclide release rates by exposing high-level waste to repository-relevant groundwater. To gain experience for the tests with spent fuel, a scoping experiment was conducted at room temperature to determine the uranium release rate from an unirradiated UO₂ powder mixture (14.3 wt % enrichment in ²³⁵U) to J-13 water under saturated conditions. Another goal set for the experiment was to develop a method for utilizing isotope dilution techniques to determine whether the dissolution rate of UO₂ matrix is in accordance with an existing kinetic model. The use of powder was intended to accelerate the dissolution process. The experiment was conducted in two cycles. Cycle 1 (161 days) was intended to stabilize the uranium release rate. In cycle 2 (93 days), the leach solution was replaced with J-13 water that was spiked with a natural uranium salt. The isotopic imbalance created by the spike caused exchange reactions that were monitored by the isotopic dilution analyses. Results of these analyses revealed unequal uranium dissolution rates from the enriched and depleted portions of the powder mixture because of undisclosed differences between them. Although the presence of this inhomogeneity has precluded the application of the kinetic model, it also provided an opportunity to elaborate on the utilization of isotope dilution data in recognizing and quantifying such conditions. Detailed listings of uranium release and solution chemistry data are presented. Uranium concentrations (17-74 μg/mL) are higher than those reported in tests with the spent fuel (0.01-10 μg/mL), probably because of a large surface area of the powder and its high oxidation level (O/U = 2.16) that could lead to the formation of soluble secondary phases (e.g., schoepite). Other problems commonly associated with spent fuel, such as the effectiveness of filtering media, the existence of uranium concentration peaks during early stages of the leach tests, the need for concentration corrections due to water replenishments of sample volumes, and experience derived from isotope dilution data are discussed in the context of the present results.

DISSOLUTION CHARACTERISTICS OF MIXED UO₂ POWDERS IN J-13 WATER UNDER SATURATED CONDITIONS

I. INTRODUCTION

Investigation of radionuclide transfer from encapsulated high-level waste (HLW) into groundwater as a function of time is being investigated by the Yucca Mountain Site Characterization Project (YMP) whose responsibility is to establish the suitability of a potential permanent HLW repository in the volcanic tuff beds near Yucca Mountain, Nevada [1]. The potential repository horizon is located 200-400 m above the water table. Unsaturated conditions are expected to prevail in the waste package during the 300-1000 year period of projected complete containment, when the package temperature will exceed the boiling point of water. During the post-containment period, however, water condensation becomes possible and, in the case of a breached container, limited quantities of water might come into contact with waste.

The YMP program at Argonne National Laboratory (ANL) overseen by Lawrence Livermore National Laboratory (LLNL) is designed to study radionuclide release rates by exposing spent Light Water Reactor (LWR) fuel to variable amounts of groundwater. To gain experience for the tests with spent fuel, a series of experiments has been conducted with unirradiated UO₂ as a substitute for the spent fuel. These experiments fall into two categories: those in which the UO₂ specimen is reacted under unsaturated conditions and those in which the specimen is completely submerged. The present study deals with an experiment of the latter category.

The saturated experiment was performed at room temperature using an enriched UO₂ powder specimen and J-13 repository-site-specific groundwater. A two cycle approach was adopted. The first cycle consisted of a conventional leaching process in which the specimen was submerged in J-13 water within a sealed stainless steel vessel. Small leachate samples were taken during this cycle to monitor changes in uranium concentration. The cycle was terminated when a steady-state concentration was reached. The termination step did not include an acid strip of the vessel, a practice that is common in spent fuel work [2]. Instead, the existing leachate was replaced with fresh J-13 water that was spiked with a natural uranium salt. Lowering the specimen into the new solution marked the beginning of the second cycle. During this cycle, the ensuing isotopic exchange reactions between the leachate and specimen were monitored as a function of time to yield kinetic data that were intended for comparing the dissolution rate of the UO₂ matrix in the specimen with those generated by an existing model [3].

The use of a powder specimen in the experiment was intended to accelerate the dissolution process. The specimen was an intimate mixture of two UO₂ powders, one depleted with respect to ²³⁵U and the other enriched, giving an overall enrichment of 14.3 wt % ²³⁵U. One of the primary goals of the experiment was to demonstrate the applicability of a mass spectrometric isotope dilution (MSID) technique in determining the dissolution rate of UO₂ in oxidizing aqueous solutions. Another goal was to gain experience in the

operating procedures for the forthcoming Spent Fuel Leaching (SFL) tests. Only a partial success for the primary goal could be achieved due to the discovery of inhomogeneities in the mixed powder specimen that prevented application of isotope exchange data to the kinetic model. The understanding gained in the nature of the exchange reactions of such a mixture, however, may find future application, because some form of inhomogeneity might occur in the spent fuel itself.

II. EXPERIMENTAL

A. Materials

The UO_2 specimen was a composite of two fine, "supersinterable" powders that were blended at a 5.58 to 1 weight ratio. The more abundant powder fraction consisted of depleted UO_2 (0.187 wt % ^{235}U) that was obtained from ANL stock (Batch No. 6-60-1089). No other analytical data to characterize this material are available. The less abundant powder fraction consisted of fully enriched UO_2 (Batch No. 2-20-8519) that was supplied by the Los Alamos Scientific Laboratory (LASL). The analyses performed at LASL show that (1) the isotopic composition of the uranium was: 1.02 wt % ^{234}U , 93.16 wt % ^{235}U , 0.406 wt % ^{236}U , and 5.42 wt % ^{238}U ; (2) the uranium assay was 87.2 wt % U; (3) the O/U atomic ratio was 2.16; and (4) the cation impurities were as shown in Table 1.

Mixing of the powders was carried out in a ballmill at ANL for an unrelated project in 1983. Approximately 3 kg of the mixture produced in this operation was placed in six polyethylene jars, which were then stored in the Special Materials vaults at ANL. One of the jars was acquired for the present work.

A partial characterization of the powder mixture was made at ANL. The isotopic distribution of uranium was measured by mass spectrometry to give: <0.0005 wt % ^{233}U , 0.1559 wt % ^{234}U , 14.312 wt % ^{235}U , 0.0651 wt % ^{236}U , and 85.467 wt % ^{238}U . The uranium assay was 87.30 wt % U, the O/U atomic ratio was 2.14, and the atomic weight of the uranium was 237.6 g-mol⁻¹. Major metallic impurities in the mixture are given in Table 1.

An x-ray diffraction (XRD) pattern of the mixed powder showed the existence of a major phase, UO_{2+x} , with a CaF_2 -type structure and a lattice parameter of 5.4677 Å. The pattern also revealed a minor, nearly amorphous phase that showed a few line correspondences with U_3O_8 . According to a study on the correlation between the lattice parameter of UO_{2+x} and its oxygen content [4], our measured parameter is equivalent to an O/U ratio of 2.034. This ratio would correspond to the presence of ~1.7 mol % of U_3O_8 , if the latter compound were the only other uranium oxide in the powder. A considerably higher oxygen content measured in the powder may indicate the presence of compounds that are richer in oxygen, such as UO_3 . For brevity, throughout this report the mixed uranium oxide will be referred to as the UO_2 powder.

Table 1. Metallic Impurities in the Enriched and Mixed UO₂ Powders

Element	Concentration ($\mu\text{g/g UO}_2$)		Element	Concentration ($\mu\text{g/g UO}_2$)	
	Enriched ^a	Mixed ^b		Enriched ^a	Mixed ^b
Al	50	<10	Mg	5	2
B	0.5	<10	Mn	<1	11
Ba	<5	<1	Mo	<3	<5
Be	<0.2	<0.5	Na	40	9
Ca	50	20	Ni	15	12
Cd	<2	<1	Pb	<1	<5
Co	<6	<2	Si	30	NA
Cr	4	<2	Sn	<1	<10
Cu	5	5	Sr	<40	<0.5
Fe	100	25	V	<3	<2
K	NA ^c	<20	Zn	<25	23
Li	<0.2	<1			

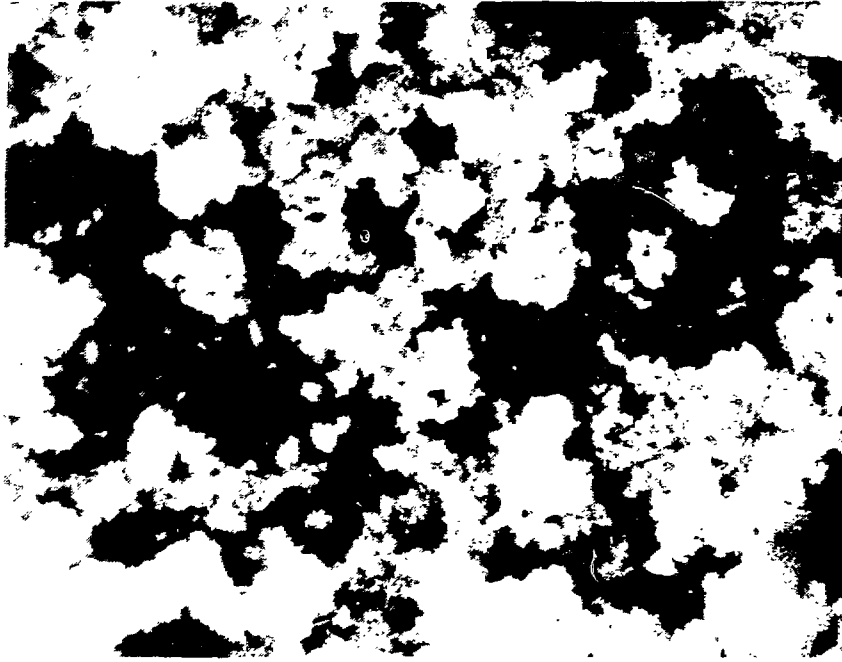
^aSpectroscopic analysis at LASL.

^bICP/AES analysis at ANL.

^cNA = Not analyzed.

An attempt was made to determine the size distribution of UO₂ particles in the powder mixture. Three methods were employed, each having a progressively higher resolution capability: (1) sieving, (2) Coulter counting, and (3) scanning electron microscopy (SEM). First, ~5 g of randomly selected powder was sifted through ten brass screen sieves ranging from 20 to 325 mesh (850 to 45 μm apertures). The largest fraction collected (73 wt %) was the one that passed through the finest sieve. That fraction was then used in the next characterization step using the Coulter counter (Coulter Electronics, Inc., Hialeah, FL). In this method, the particles are suspended in a stirred electrolyte solution and are counted on the volume basis as they pass through a tube whose aperture is selected for an appropriate particle range, 1 to 40 μm in this case. The results, averaged over six runs, showed that 88% by volume of the particles fell within the 6 to 10 μm range. The third method used was an SEM examination of an unsifted powder sample. The resulting micrographs are shown in Fig. 1. They reveal cloud-like images that appears to be made of clusters of very fine particles ($\ll 0.1 \mu\text{m}$). Therefore, one is led to conclude that the material handled in the above sifting and counting operations may have been made up of sintered agglomerates of UO₂ particles and that the actual size distribution of these particles is unknown. It is also noteworthy that no evidence was found during any of these operations to indicate the existence of any physical differences between the powder fractions.

(a)



(b)

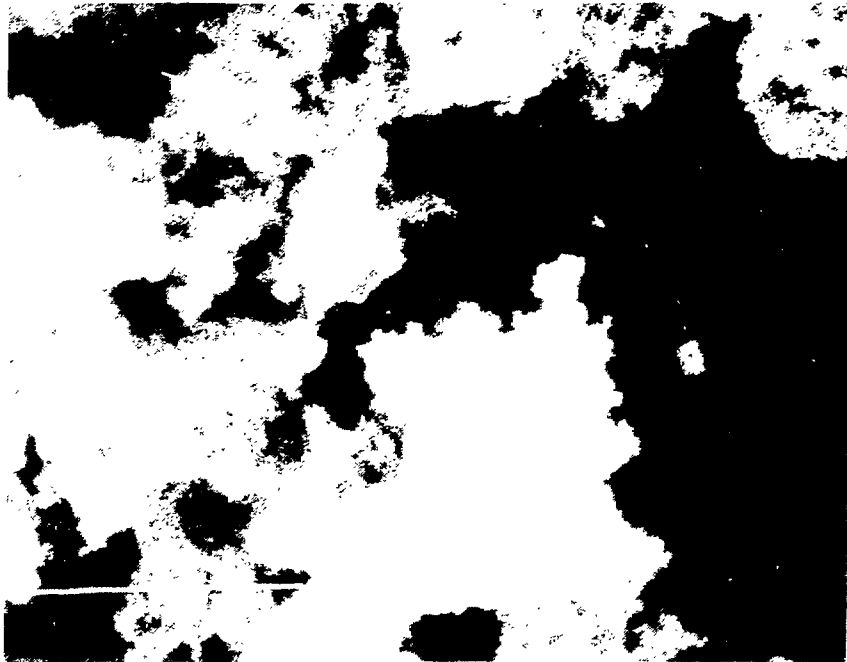


Fig. 1. SEM Photomicrographs of UO_2 Powder Mixture (a) 1000X, (b) 5000X.

In a recent study [5], the crystallite sizes of UO_2 powder samples have been determined from the Fourier analysis of XRD patterns. The samples were prepared by pyrohydrolysis and subsequent reduction of ammonium uranyl carbonate (AUC) powder, which is a common source of sinterable powders used in UO_2 pellet production [6]. For an O/U ratio of 2.12, the mean crystallite size was found to be 70 nm, a result that supports our conclusion.

The chemistry of water plays an important role in radionuclide leaching of a waste form. The water used in the present study came from well J-13, which is located to the east of Yucca Mountain, NV, and whose water chemistry is similar to that found in drillholes from below the water table at Yucca Mountain [7]. Because the actual composition of the repository pore fluid is not known, the J-13 water has been adopted as a reference water for the YMP project. The J-13 water for our experiments was supplied by the Lawrence Livermore National Laboratory (LLNL). Composition determined at ANL is presented in Table 2. The data for the drillhole samples [7] and for an averaged sample measured at LLNL [8] are also included in Table 2. Deionized water (DIW) used throughout the present experiment had a resistivity of >18 megohm-cm.

Ultrax grade nitric acid, used for the acidification of samples being prepared for the uranium and cation analyses, was purchased from the J. T. Baker Chemical Company, Phillipsbury, NJ. Uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (F.W. = $502.13 \text{ g}\cdot\text{mol}^{-1}$), used in making the spiking solution, was prepared from National Bureau of Standards (NBS) Standard Sample 950a (U_3O_8), which is a certified uranium assay standard of natural isotopic composition. A portion of the standard material was heated in air at 900°C for one hour to assure complete oxidation, cooled in a dessicator, weighed, dissolved in 4 mL of 50% HNO_3 , and evaporated to dryness on a steam bath to produce the crystalline product.

B. Apparatus

A schematic diagram of the experimental setup is shown in Fig. 2. It consisted principally of a stainless steel vessel and its ancillary parts. The apparatus was fabricated at the Pacific Northwest Laboratory (PNL) according to a design that had been used for the spent fuel dissolution test at PNL [2]. The UO_2 powder specimen was contained in a basket that was equipped with a bailed handle to facilitate its placement under water. (The rings on the bail were originally intended for supporting spent fuel cladding hulls and had no function in the present experiment.)

The experiment was performed with 250 mL of J-13 water. Changes in the liquid level were monitored to within ± 1 mm with a hollow float attached to an indicator wire. The vessel was sealed with a threaded cap. The matching male thread on the vessel was chrome-plated to prevent galling. The cap had two ports: (1) a sampling port that was opened for brief periods to aerate the solution, retrieve solution samples, and replenish the

Table 2. Composition of J-13 Water

Constituent	Concentration, $\mu\text{g/mL}$		
	This Study	Kerrisk ^a	LLNL ^b
Na	48	45	43.9
Si	34.2	30.0	27.0
Ca	14.1	11.5	12.5
K	5.3	5.47	5.11
Mg	2.3	1.73	1.92
Li	<0.1	ND	0.042
Fe	<0.1	0.044	0.006
Al	<1	0.026	0.012
SO ₄ ⁻²	18	18.1	18.7
NO ₃ ⁻	5.1	10.1	9.6
Cl ⁻	7.7	6.4	6.9
F ⁻	2.3	2.1	2.2
NO ₂ ⁻	DL	ND	ND
C(org)	4.1	ND	ND
C(inorg)	19.6	28.1	24.6
pH	8.4	7.0	7.6

^aFrom [7].

^bAverage of LLNL supply of J-13 water, from [8].

ND = Not determined.

DL = Concentration at the detection limit.

removed portion of the solution with J-13 water; and (2) a port for the sight tube which was to house the solution level indicator wire. A better contrast for the level readings was achieved by sliding a TeflonTM sleeve with a cut-out front window over the sight tube. All seals were made using ethylene propylene O-rings and the threaded joints were tightened by hand. All apparatus components were made of 304L stainless steel, except for the sight tube which was made of fused silica. The experiment was performed in a ventilated Blickman hood.

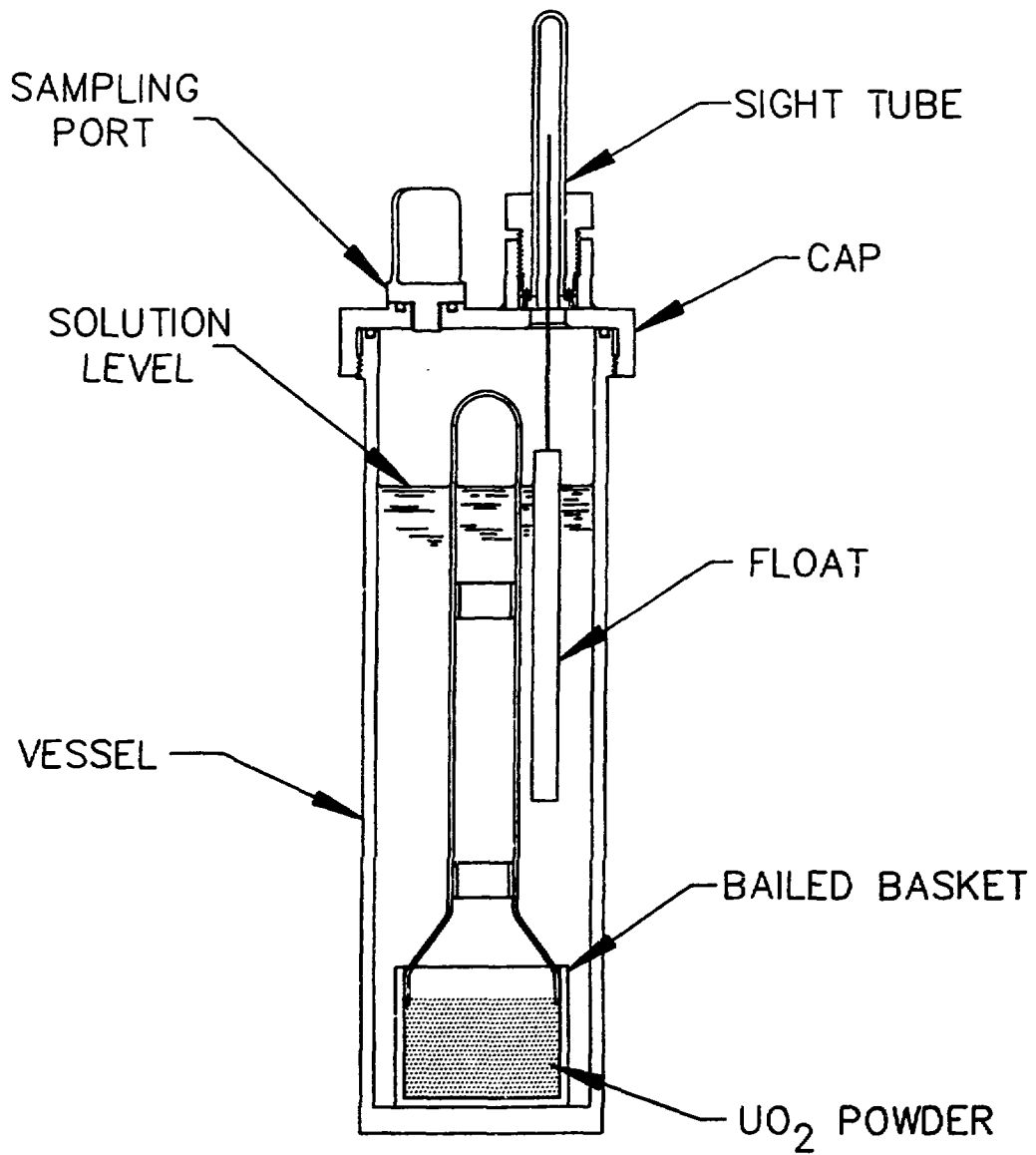


Fig. 2. Schematic Diagram of the Apparatus.

C. Sampling Equipment

Filtered and unfiltered samples were taken from the leachate solution. The origin and characteristics of the filters were as follows:

(1) 0.4- μm pore size, 13-mm-dia. polycarbonate membranes with plastic holders (Nuclepore Corporation, Pleasanton, CA); and (2) CF25 and CF50A membrane cones (Amicon Corporation, Danvers, MA) with 25,000 and 50,000 molecular weight cut-offs that correspond nominally to 18 and 36 \AA pore sizes, respectively. Amicon filters had conical supports and the filtration required 10-min centrifuging periods at 1300 rpm using a horizontal rotor.

D. Procedure

The first cycle was initiated by pouring 250 mL of J-13 water into the vessel. Approximately 80 g of UO_2 powder was placed in the bailed basket, which was then slowly lowered into the vessel to commence the leaching process. There was some bubbling from the powder during the insertion, but no noticeable extraneous matter rose to the water surface. The vessel cap was assembled by installing the sight tube and the sampling port plug. After adding the float, the cap was positioned to guide the float wire into the sight tube hole and was slowly rotated to make a hand-tight seal (~10 ft-lb torque). The assembled vessel was then placed on a level surface in a Blickman hood until sampling time.

Small samples of the leachate were taken at approximately weekly intervals for the pH, carbon, uranium, and ionic composition determinations. The sampling procedure was as follows. After removal of the sampling port plug, six consecutive 10-mL portions of air were slowly injected into the leachate to aerate and mix the fluid at a needle point level that was ~1 cm above the powder specimen. Leachate samples were then taken according to the matrices given in Tables 3 and 6 of Section III. The volume of the removed leachate was immediately replenished with fresh J-13 water. After the sampling plug has been replaced, the fluid level was verified by recording float wire position and the vessel was put aside until the next sampling date.

The pH measurement (1-mL sample) and carbon analysis (1-mL sample) were carried out immediately after sampling to minimize contamination by atmospheric CO_2 . A 4-mL sample for the anion analysis was also submitted without treatment. For the cation analysis, a 2.5-mL sample was submitted after dilution to 25 mL with 2% HNO_3 . One-mL samples for the uranium analysis were submitted in both filtered and unfiltered modes. Three types of filter were employed: 0.4 μm Nuclepore membranes, 36 \AA Amicon CF50A cones, and 18 \AA Amicon CF 25 cones. A special procedure was followed for the Amicon filters. First, the cone was presoaked for 2 h in DIW and spun for 10 min in the centrifuge to rid it of excess water. It was then conditioned by adding 1 mL of the leachate, centrifuging, and discarding the filtrate. This step was repeated with another 1-mL leachate sample, this time saving the filtrate for analysis. All samples destined for the uranium analyses were acidified with three drops of concentrated HNO_3 as a precaution against heavy-nuclide plate out.

Cycle 1 was terminated after 161 days by (1) removing the vessel cap and the float, (2) lifting the basket out of the vessel, (3) removing all accessible leachate solution from the vessel and basket, and (4) temporarily storing the basket plus specimen in a covered container. Total quantity of the fluid removed was 224 mL, the remaining 26 mL being retained by the powder. The specimen within the basket appeared as a wet, brownish-black mass. The portion directly below the sampling port opening had an ~1 cm deep erosion hole from air injections during the sampling. Some of the powder remained suspended in the fluid phase or deposited on the vessel bottom, but the amount was considered to be negligible when compared with the bulk of the specimen. All vessel parts except for the basket and its contents were rinsed with DIW and dried.

The spiked leachate needed for cycle 2 was prepared by dissolving $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals containing 16.28 mg of natural uranium in 275 mL of J-13 water, thus giving a concentration of 59.2 $\mu\text{g U/mL}$. This concentration was chosen because it coincided with the essentially constant analytical data taken at the end of cycle 1. The value is in good agreement with the MSID analysis performed on an unfiltered sample of the spiked leachate that gave a concentration of 58.5 $\mu\text{g U/mL}$ and an isotopic distribution of 0.0048 wt % ^{234}U , 0.710 wt % ^{235}U , 6 wt % ^{236}U , and 99.285 wt % ^{238}U . Approximately 200 mL of the spiked leachate was added to the vessel.

Cycle 2 was initiated by (1) lowering the basket containing the wet specimen into the vessel, (2) immediately replacing the float and the cap assembly (less the sampling port plug), (3) adding additional spiked leachate to reach the previously established float level, and (4) replacing the sampling port plug. The sampling procedure was identical to that of cycle 1 except for the following changes. In most cases, the sample volumes were restricted to 2-3 mL in order to minimize the dilution effect due to the leachate replenishment with J-13 water after each sampling. The analyses were also restricted to uranium only and to samples that were filtered through CF25 cone membranes. Only for the penultimate sample of cycle 2, the volume was increased to 11 mL and a full complement of analyses was performed. The frequency of sampling was increased to accommodate high isotopic exchange rates. Finally, the uranium was analyzed exclusively by the MSID method to determine both the total uranium and its isotopic distribution.

III. RESULTS

Cycle 1 of the experiment was completed after 161 days. The data for the uranium analyses are presented in Table 3. The filters used were the Nuclepore 0.4- μm membranes, which are expected to remove the particles but not colloids, and two Amicon cone membranes (CF50A and CF25), which remove both the particles and colloids [9]. The uranium determinations were performed either by laser-excited fluorescence (Scintrex) or by MSID, depending on the instrument availability. The latter method is preferable because of its superior accuracy ($\pm 0.5 \mu\text{g U/mL}$).

Table 3. Uranium Sampling and pH Data for Cycle 1

Elapsed Time (days)	Sample Size (mL)	pH	Total Uranium Concentration ($\mu\text{g/mL}$)							
			Unfiltered		0.4 μm Filter		CF50A Filter		CF25 Filter	
			Scintrex	MSID	Scintrex	MSID	Scintrex	MSID	Scintrex	MSID
0	0	8.4								
1	2		31	31.5						
7	2		48	49.2						
14	2		57	68.4						
21	3		71		75	72.2				
28	5	6.5	84		84				36	33.8
35	15	6.5	105		103				56	
42	3	6.5	104						40	34.9
49	5	6.2	118						66	
56	5	6.1	139						75	64.2
63	5	6.1	152						81	
71	12	5.9	163		163				97	89.4
77	5	6.1	163						57	
84	6	6.0	188				83		61	55.2
91	6	6.2	160				61		72	
98	7	6.0		155					111	65.8
105	12	6.0		158					95	64
112	7	6.1		151					64	72.7
119	6	6.1		144					70	70
126	7	6.0		147					69	72.1
133	6	5.9		147					64	67
140	13	6.2		140					64	74.0
147	6	6.3		146					57	74
161	13	6.0	188				74		53	50.9

Inspection of Table 3 reveals that there is no difference in the data between the unfiltered and 0.4- μm -filtered samples. This indicates that the suspended particle diameters are smaller than 0.4 μm in agreement with the conclusion reached from the particle distribution experiments discussed in Section II. Similarly, with few exceptions there is little difference in the filtering action between the CF50A and CF25 cone membranes, the latter membrane on the average being only slightly more efficient. This comparison reassures the adequacy of CF25 filter, which was used as the sole filtering agent in the subsequent samplings. A plot of uranium concentrations in the leachate as a function of time is shown in Fig. 3a, where the CF25 filter results are limited to those obtained using the MSID technique. The unfiltered and CF25-filtered data show parallel patterns, the values of the former data being approximately twice as large as the latter ones. In both cases there are maxima reached in the 50-100 day period, followed by steadier concentration patterns. Such behavior has been reported earlier in the spent fuel leaching tests [2] and has been attributed to higher dissolution rates from oxidized surface films than those from bulk specimens. Higher uranium concentrations in the unfiltered samples are probably due to the presence of particulate matter that was dissolved upon sample acidification before the analysis. Some particles were visually observed in the unused portions of unacidified leachate samples.

The volumes of the leachate that are replaced with pure J-13 water after each sampling are plotted on the bottom of Fig. 3a. The presence of dilution effects on the uranium concentration caused by the water replenishments is highlighted by two large samples taken on days 35 and 71, where the uranium concentration on the following sampling period is much lower than expected. A correction for this dilution effect can be applied to all points of the plots in Fig. 3a by adding the quantity $(V_{i-1}/250) \cdot C_{i-1}$ to the concentration C_i of each point, where i and $(i-1)$ are the indices of the current and previous points, respectively, C is the uranium concentration in $\mu\text{g}/\text{mL}$, and V is the volume in mL of water added. The effect of these corrections is shown in Fig. 3b.

In addition to the pH and uranium determinations, larger leachate samples were taken at certain intervals to include analyses for carbon, anions, and cations. The results of these analyses, together with those of the starting J-13 water, are shown in Table 4. The following assessment can be made of the data taken during the 1-161-day period: (1) the pH values show an initial drop and then level off at ~ 6.0 , (2) the total organic carbon (TOC) undergoes a slight rise and reaches a plateau at $\sim 8 \mu\text{g}/\text{mL}$, (3) the total inorganic carbon (TIC) shows a steep descent from 19.7 to 2.3 $\mu\text{g}/\text{mL}$, (4) the NO_3^- concentration shows a slight initial increase followed by a gradual decline to near the starting value, (5) anions other than HCO_3^- and NO_3^- tend to retain their values of pure J-13 water, (6) concentrations of major cations (Na, Si, Ca, and K) show significant initial decreases, presumably because of their participation in the formation of secondary phases, and (7) minor cations (Mg, Al, and B) remain near their initial low values. A graphic representation of selected analytical results is given in Fig. 4.

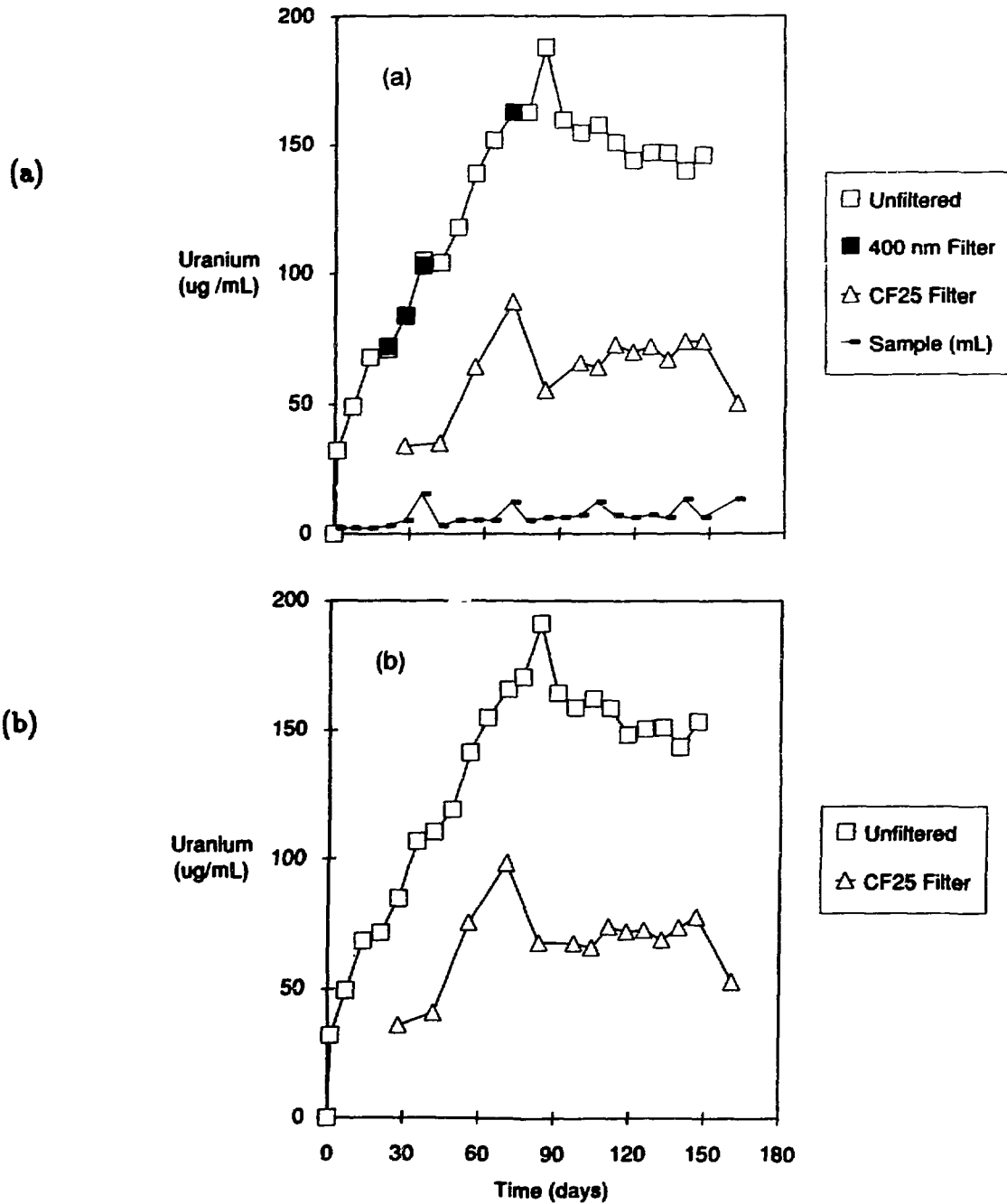


Fig. 3. Filtering Effects on the Uranium Concentrations in the Leachate Samples of Cycle 1. (a) As analyzed, (b) corrected for dilution.

Table 4. Solution Compositions for Cycles 1 and 2

Type of Analysis	J-13 Water	Cycle 1					Spiked J-13	Cycle 2		
		Day 35	Day 71	Day 105	Day 140	Day 161		Day 0 ^a	Day 26.2	
pH	8.4	6.5	5.9	6.0	6.2	6.0	8.2	8.0	7.2	
Carbon ($\mu\text{g/mL}$)	TC	23.8	14.9	12.4	11.1	9.7	9.8	20.7	19.6	9.6
	TOC	4.1	9.6	9.2	8.0	7.4	7.5	3.3	3.7	4.5
	TIC	19.6	5.3	3.2	3.1	2.3	2.3	17.4	15.9	5.1
Anions ($\mu\text{g/mL}$)	HCO ₃ ⁻	99.6	26.9	16.3	15.8	11.7	11.7	88.5	80.8	25.9
	F ⁻	2.3	2.7	2.3	2.0	1.9	1.8	2.6	2.5	1.9
	Cl ⁻	7.7	7.9	7.4	7.4	7.4	6.8	7.2	7.2	7.5
	NO ₃ ⁻	0.1	8.0	8.4	7.9	7.8	6.2	41.	37.	36.
	NO ₂ ⁻	DL ^b	<1	<1	<1	<1	<1	<1	<1	<1
	SO ₄ ⁻²	18.	18.	18.	18.	18.	18.	17.	20.	20.
Cations ($\mu\text{g/mL}$)	Na	48.0	18.6	15.8	15.6	13.7	14.5	54.3	50.2	31.7
	Si	34.2	14.9	15.7	14.7	15.9	16.3	31.1	29.6	23.0
	Ca	14.1	3.5	2.6	2.9	2.9	2.7	14.0	12.8	3.6
	K	5.3	<3	<3	<3	<3	<3	4.7	<3	<3
	Mg	2.3	3.9	3.8	3.7	3.6	3.3	2.5	2.6	2.3
	Al	<1	<1	1.3	1.3	1.4	1.4	<1	<1	<1
	B	<0.3	0.3	1.9	1.7	1.8	1.1	1.1	1.1	1.1

^aEstimated values (see text).

^bDL = Concentration at the detection limit.

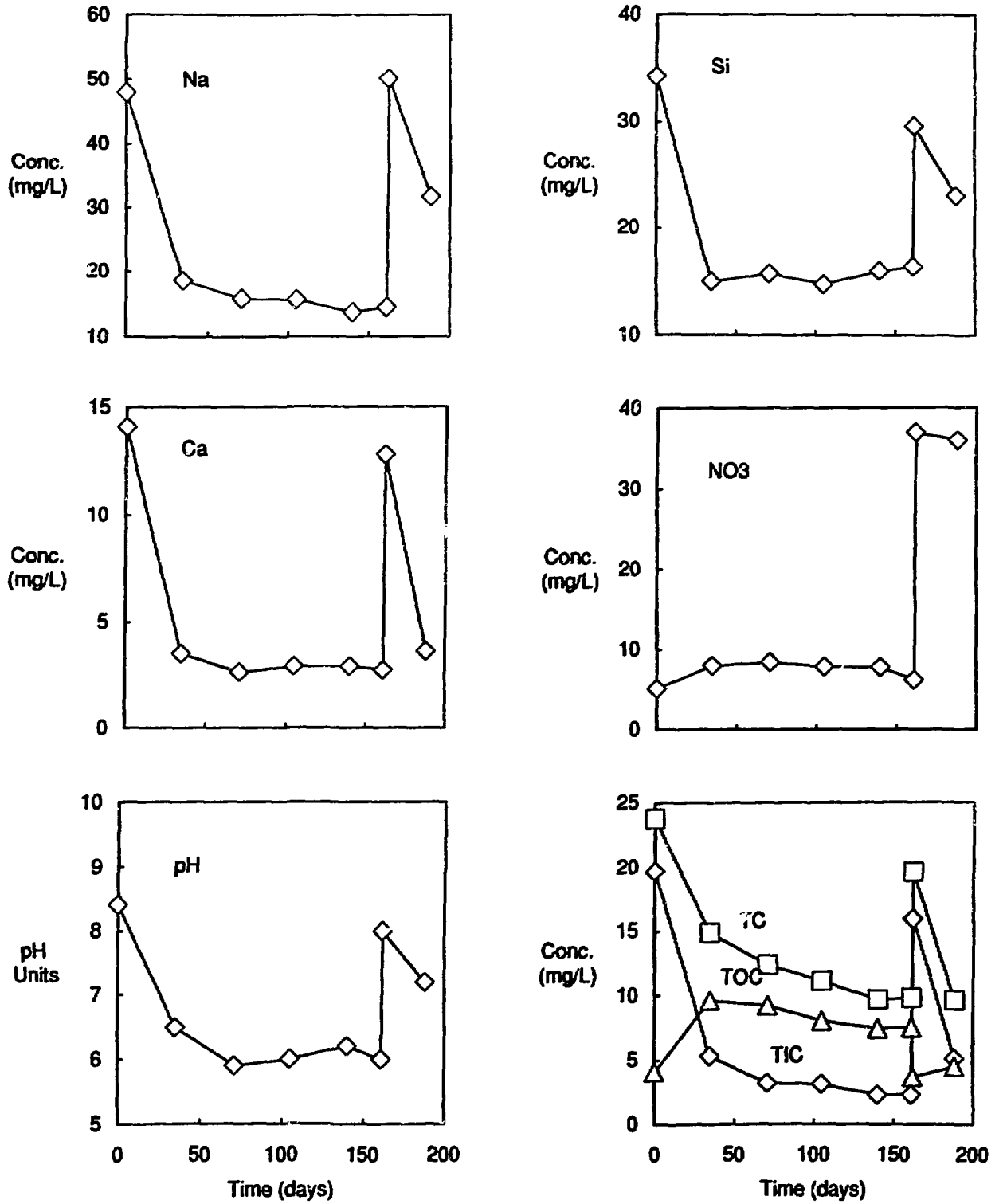


Fig. 4. Time Dependence of pH and Ionic Concentrations in Leachate Solutions During Cycles 1 and 2.

The leachate for cycle 2 was formed when the basket containing the UO_2 specimen, soaked with 26 mL of fluid from cycle 1, was immersed in 224 mL of spiked solution. Because all cycle 2 samples for uranium determination were filtered through CF25 cone membranes, it is important to estimate the initial uranium concentration of the leachate calculated as if it were filtered in the same manner (see next paragraph). For the 26-mL portion of the leachate originating from cycle 1, one can take the average value of the CF25-filtered MSID data listed in Table 3 for the 98-161 day period, namely 67.8 $\mu\text{g/mL}$.

To determine the CF25-filtered uranium concentration in the 224-mL portion of the leachate originating from the spiked solution, the following side experiment was performed. Four spiked solution samples were subjected to different filtration modes according to the matrix in Table 5. After acidification with three drops of concentrated HNO_3 , each sample was submitted for an MSID analysis to determine the total uranium and its isotopic makeup. As before, the results in Table 5 show no difference between the unfiltered and 0.4- μm -filtered samples, but significantly lower concentrations occur in samples filtered through the cone membranes. For example, a

Table 5. Effect of Filtering on the Uranium Isotope Distribution and Total Uranium Concentration for a Solution of Natural Uranyl Nitrate Hexahydrate in J-13 Water

Filter	Uranium Isotope Distribution (wt %)				238/235 Ratio	Total U ($\mu\text{g/mL}$)
	U-234	U-235	U-236	U-238		
None	0.0049	0.7109	0	99.284	139.7	58.5
Polycarbonate Membrane 0.4 μm	0.0052	0.7116	0	99.283	139.5	58.8
Amicon Cone CF50A	0.0051	0.7115	0	99.283	139.5	42.3
Amicon Cone CF25 (Filtered Once)	0.0053	0.7117	0	99.283	139.5	40.2
Amicon Cone CF25 (Filtered Twice)	0.0050	0.7113	0	99.284	139.6	36.5

reduction in the concentration between the unfiltered and CF25-once-filtered modes amounts to 31%. One may conclude that in clear, dilute solutions prepared in glass containers the uranium can form colloidal species and that the presence of solid UO_2 phases is not a necessary condition for such a formation. As is expected for a homogeneous medium, the uranium isotope distribution is not affected by the filtration processes. Using the data in Table 5 the concentration of the 224-mL portion of the leachate can now be calculated to be $(26/250)(67.8) + (224/250)(40.2) = 43.1 \mu\text{g/mL}$. This value was taken to represent the starting uranium concentration for cycle 2.

High initial isotope exchange rates anticipated at the beginning of cycle 2 were taken into account by selecting sharply graduated sampling intervals so that they ranged from 1 hour to 67 days according to the matrix given in Table 6. Most sample volumes were limited to 2 mL, which is the minimum amount needed to perform a meaningful filtration through a CF25 cone membrane. These volumes were considered to be small enough not to require leachate dilution corrections. The pH measurements shown in Table 6 were carried out on the 1-mL sample portions that were used for conditioning the cones (see Section II-D). It is noteworthy that the steadily declining pH values fit almost exactly into the 0 to 28-day span that was left blank during the first cycle (see Table 3 and Fig. 4).

Table 6. Sampling Data for Cycle 2

Sampling Interval (hours)	Elapsed Time (days)	Sample Size (mL)	pH	Uranium Concentration ($\mu\text{g/mL}$)
0.0	0.000	0	8.0 ^a	43.1 ^a
1.1	0.044	2	8.1	31.6
2.0	0.129	2	8.1	31.4
3.9	0.290	2	8.1	25.9
6.9	0.578	2	8.1	28.5
13.3	1.133	2	8.0	33.1
24.0	2.135	2	7.9	20.7
23.7	3.124	2	7.8	19.3
48.3	5.135	2	7.7	18.7
72.0	8.133	2	7.7	18.6
96.1	12.137	2	7.6	17.5
337.3	26.192	11	7.2	25.2
1606.5	93.130	3	6.4	34.0

^aEstimated value (see text).

The uranium concentrations for cycle 2 undergo some initial scatter, go through a minimum on the twelfth day, and appear to begin the slow ascent to some steady-state value. Because of the large solid specimen mass, such a value is likely to be in common with the steady-state value that would have been reached during cycle 1 if it were allowed to continue.

During cycle 2, all uranium analyses were performed using the MSID method. In addition to providing the uranium assays, the method yielded data on the distribution of principal uranium isotopes in the solution samples. These data are presented in Table 7. The isotopic imbalance between the dissolved uranium in the spiked leachate and solid UO_2 specimen has set off rapid isotope exchange reactions. The course of these reactions was monitored by taking leachate samples for MSID analyses. As can be seen from the variation of $^{238}\text{U}/^{235}\text{U}$ ratio with time in Table 7, an unexpected trend appeared in the isotopic distribution. This ratio was expected to decrease from 25 at the start of cycle 2 to that of the mixed powder itself (5.97), but the decrease has continued past this value reaching 2.27 on day 93. The trend was verified by performing MSID analyses on selected archived leachate samples from cycle 1. As shown in Table 7, here too the $^{238}\text{U}/^{235}\text{U}$ ratio did not stay constant at 5.97 but gradually decreased to a value of 2.23. It is clear that these changes in the isotopic distribution must stem from inhomogeneities inherent in the powder specimen. (This subject will be more fully discussed in Section IV.) In addition to the leachate solution data, Table 7 also lists available isotopic compositions of the powders.

The ionic solution concentrations for cycle 2 are based on a single full-range analysis performed on the 26.2-day sample. Analytical results are given in Table 4 where they can be compared with those of cycle 1. The values in the starting leachate of cycle 2 are given in column 9 of that table. As was done before for the uranium, they were estimated by adding the values representing the 24-mL portion due to final leachate of cycle 1 (column 7) to those representing the 224-mL portion of the spiked solution (column 8). Each pair of data was weighted by their respective factors, 26/250 and 224/250. In all cases, the differences between the initial and 26.2-day samples of cycle 2 parallel those of cycle 1 at the corresponding time periods. The case of NO_3^- is different in that the large excess of this anion introduced with the $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ spike was still retained after 26.2 days (see Fig. 4). One can anticipate, however, that after a longer period of time this and other ions would have established concentrations that are commensurate with those imposed by the powder specimen. Such a trend is indicated in cycle 1 data.

IV. DISCUSSION

The kinetic model for calculating the dissolution rate of UO_2 matrix from MSID data obtained for the spiked solutions is applicable only to homogeneous solid specimens [3]. Thus, if a two-cycle experiment were performed on such a specimen, the distribution of uranium isotopes in the leachate during cycle 1 would remain unchanged from that of the solid specimen. For cycle 2, the isotopic exchange reactions due to the initial perturbation by the spike would eventually subside and the distribution would again return to that of the solid specimen.

Table 7. Distribution of Uranium Isotopes and D/E Ratios in Solid UO_2 and in Leachate Samples for Cycles 1 and 2

Phase	Elapsed Days	Uranium Isotope Distribution (wt %)				238/235 Ratio	X_d/X_e Ratio ^a
		U-234	U-235	U-236	U-238		
Depleted UO_2 Powder	NA ^b	c	0.187	0	99.807 ^d	533.73 ^d	NA ^b
Enriched UO_2 Powder	NA ^b	1.02	93.16	0.406	5.42	0.05818	NA ^b
Mixed UO_2 Powder	NA ^b	0.1559	14.312	0.0651	85.467	5.9717	5.5820
CYCLE 1 Leachate Solutions	1.00	0.2008	18.38	0.0809	81.338	4.4254	4.1107
	7.00	0.2062	18.96	0.0850	80.753	4.2601	3.9537
	14.00	0.2126	19.42	0.0870	80.280	4.1338	3.8337
	21.00	0.2282	20.96	0.0936	78.719	3.7559	3.4759
	28.00	0.2467	22.54	0.1004	77.115	3.4216	3.1595
	42.00	0.2705	24.73	0.1104	74.885	3.0276	2.7373
	56.00	0.2846	26.09	0.1162	73.513	2.8181	2.5897
	71.00	0.2931	26.87	0.1193	72.717	2.7062	2.4843
	84.00	0.3027	27.83	0.1219	71.749	2.5785	2.3641
	98.00	0.3112	28.53	0.1270	71.029	2.4893	2.2799
	112.00	0.3187	29.17	0.1293	70.383	2.4129	2.2079
	126.00	0.3240	29.65	0.1317	69.899	2.3579	2.1560
	140.00	0.3282	30.06	0.1331	69.474	2.3109	2.1118
161.00	0.3349	30.78	0.1359	68.750	2.2336	2.0392	
CYCLE 2 Leachate Solutions	162.00	0.0393	3.844	0.0142	96.102	25.001	(2.0399)
	167.04	0.0396	3.846	0.0140	96.101	24.988	(2.0398)
	162.13	0.0483	4.631	0.0173	95.304	20.581	(2.0396)
	162.29	0.0640	6.055	0.0241	93.856	15.449	(2.0391)
	162.58	0.0788	7.403	0.0298	92.489	12.494	(2.0384)
	163.13	0.0937	8.783	0.0362	91.087	10.371	(2.0369)
	164.14	0.1355	12.58	0.0534	87.230	6.9337	(2.0343)
	165.12	0.1515	14.03	0.0601	85.761	6.1139	(2.0317)
	167.13	0.1729	15.95	0.0683	83.809	5.2544	(2.0265)
	170.13	0.1940	17.81	0.0772	81.914	4.5982	(2.0190)
	174.14	0.2274	20.85	0.0916	78.831	3.7808	(2.0092)
	188.19	0.2697	24.70	0.1080	74.927	3.0340	(1.9771)
	255.13	0.3315	30.42	0.1340	69.114	2.2719	(1.8608)

^aNumbers in parentheses indicate values extrapolated from Cycle 1 data.

^bNA = Not applicable.

^cData not available.

^dEstimated value.

The powder mixture selected for the present experiment appeared to have properties that were indicative of a homogeneous material, e.g., both powders had identical oxidation levels and no distinction could be made between the powders by examining SEM micrographs. The decline in the $^{238}\text{U}/^{235}\text{U}$ ratio well below the 5.97 value of the powder mixture, however, has indicated the existence of a homogeneity problem in the specimen. It is clear from the data that the enriched portion of the powder had a significantly higher dissolution rate in J-13 water than the depleted portion, owing to some undisclosed difference between the powders. The inhomogeneity of the specimen was discovered from MSID data, which were first obtained during cycle 2, i.e., well into the latter portion of the experiment. The work was continued to its conclusion to preserve the great deal of information being generated by the experiment. The presentation of that information is the main purpose of this report. The utility of the MSID method in detecting the existence and extent of specimen inhomogeneity is discussed in the following paragraphs.

For cycle 1, in which UO_2 powder is leached in pure J-13 water, the dissolved uranium in the leachate can be thought of as being composed of two portions: one originating from depleted powder, the other from enriched powder. Isotopic distribution data given in Table 7 allow calculations of the depleted/enriched weight ratios (X_d/X_e) in dissolved uranium. For example, consider four principal uranium isotopes in the sequence ^{234}U , ^{235}U , ^{236}U , and ^{238}U . The concentration of the i th isotope in the mixed uranium solute, $C_{m,i}$ (in g/100 g U), can be written as

$$C_{m,i} = X_{d,i}C_{d,i} + X_{e,i}C_{e,i} \quad (1)$$

where $X_{d,i}$ and $X_{e,i}$ are the weight fractions of the i th isotope in the depleted and enriched powders, respectively; $C_{d,i}$ and $C_{e,i}$ are the concentrations (in g/100 g U) of the i th isotope in the depleted and enriched portions of solid powder mixture, respectively; and $i = 1, 2, 3,$ and 4 is the isotope sequence index. Since $X_{d,i} + X_{e,i} = 1$, Eq. 1 can be rewritten as

$$\left(\frac{X_d}{X_e} \right)_i = \left(\frac{C_e - C_m}{C_m - C_d} \right)_i \quad (2)$$

Because of random errors in the analytical data, there is a slight variation ($\pm 0.5\%$) in the $(X_d/X_e)_i$ values, calculated for each isotope at a given sampling period. An average ratio can be determined using weighting factors $X_{m,i}$ according to the following equation

$$\frac{X_d}{X_e} = \sum_{i=1}^4 \left(X_m \frac{C_e - C_m}{C_m - C_d} \right)_i \quad (3)$$

where $X_{m,i} = C_{m,i} / \sum_1^4 C_{m,i}$ is the weight fraction of the *i*th isotope in the mixed uranium solute. Equation 3 was employed to calculate the X_d/X_e ratios for the mixed UO_2 powder and for the leachate solution of cycle 1. They are listed in column 8 of Table 7.

The apportionment of the dissolved uranium into the depleted and enriched fractions, applied to the leachate solution of cycle 1, does not lend itself to the spiked leachate of cycle 2. Here, the uranium introduced with the spike bears no relationship to the powder specimen and there is no information on the isotope exchange rates between the new leachate and individual powder fractions. Therefore, Eq. 3 cannot be applied to the isotopic distribution data of cycle 2. Instead, it was assumed that, owing to the great bulk of solid specimen, X_d/X_e ratios will continue to change at a rate established during cycle 1. These cycle 1 ratios, extrapolated into cycle 2 by the least-squares method, are also listed in column 8 of Table 7.

The isotopic distribution in the depleted, enriched, and mixed powders for the principal uranium isotopes (^{235}U and ^{238}U) is shown in Fig. 5, where the weight percent of each isotope with respect to total uranium is plotted against time. Since the concentration of the *i*th isotope in the depleted and enriched powders is given by $C_{d,i} = X_d C_{m,i}$ and $C_{e,i} = X_e C_{m,i}$, respectively, these plots were generated from $C_{m,i}$ and X_d/X_e data of Table 7. The positive slope of the ^{238}U curve in the center plot provides verification that the dissolution rate of the enriched powder is considerably higher than that of depleted powder. Asymptotic approaches of cycle 2 curves to the lines extrapolated from cycle 1 indicate that, after a reasonably short time period (~150 days), the effects of the spike become negligible. It must be stressed that cycle 2 curves for the depleted and enriched powders were calculated using X_d and X_e weight fractions that are associated with cycle 1. The assumption of this idealized version is not necessarily correct and the actual shape of the curves might be different. This is the principal reason that makes cycle 2 isotopic exchange data unsuitable for kinetic model calculations.

Total uranium concentrations reported for CF25-filtered samples in Tables 3 and 6 (17-74 $\mu\text{g/mL}$) are much higher than those reported for the leach tests with spent fuel [2] (0.01-10 $\mu\text{g/mL}$). A plausible explanation for this observation is provided by the higher dissolution rates that would be expected from the large surface area of the powder. Another probable reason is that a relatively high oxidation level of the powder ($O/U = 2.16$) could lead to the formation of soluble minerals.

According to a simulation study using EQ3/6 geochemical model on the dissolution of 100 g of spent fuel in 1 kg of J-13 water at 25°C [3,10], several uranium-bearing minerals were found to play a role in controlling the uranium concentration in the leachate: haiweeite [$Ca(UO_2)_2Si_6O_{15} \cdot 5H_2O$, 0.015-0.024 $\mu\text{g U/mL}$ solubility range], soddyite [$(UO_2)_4(SiO_4)_2 \cdot 4H_2O$, 0.03-12 $\mu\text{g U/mL}$], and schoepite [$UO_3 \cdot 2H_2O$, 15 $\mu\text{g U/mL}$]. The model

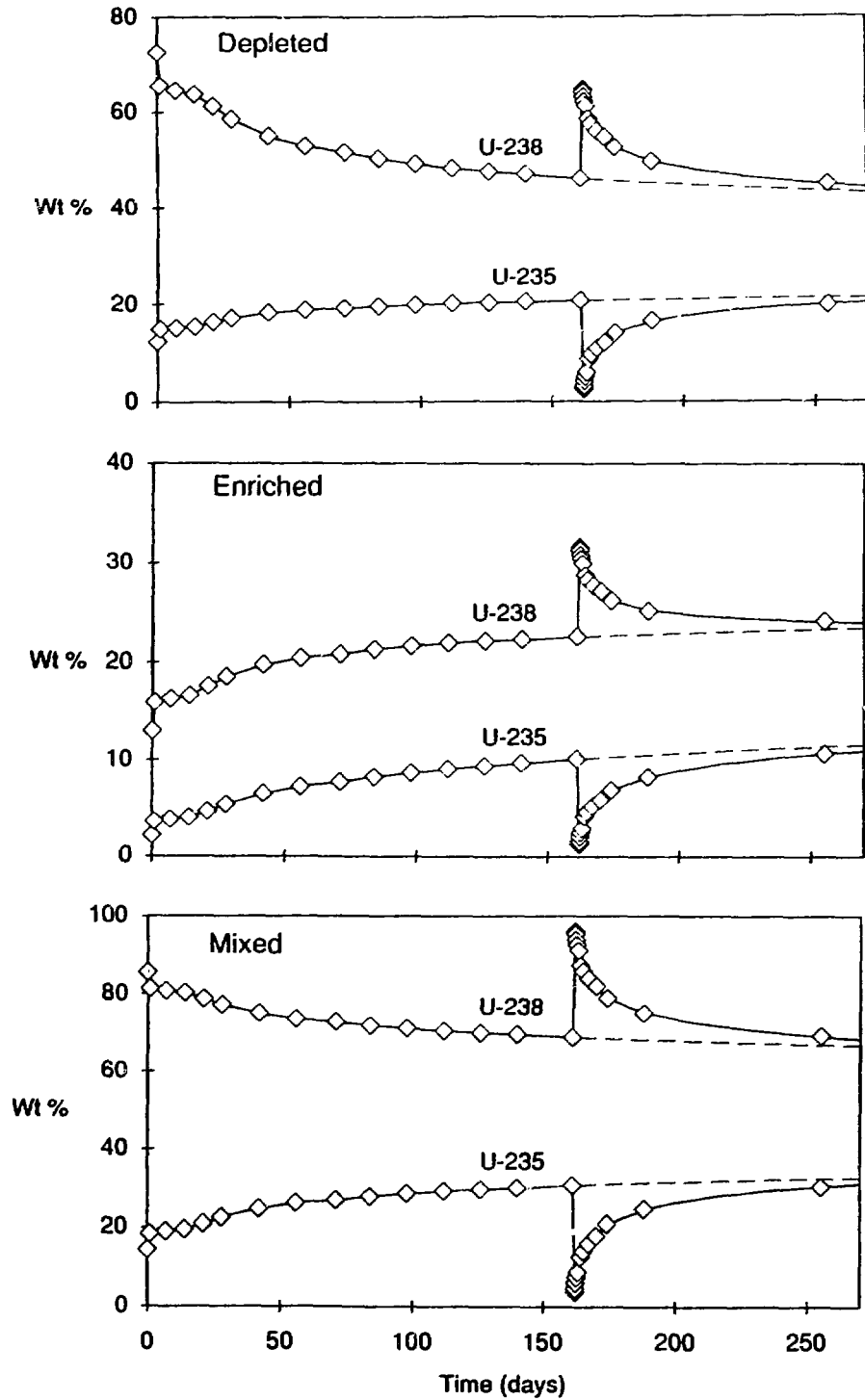


Fig. 5. Distribution of ^{235}U and ^{238}U in the Depleted, Enriched, and Mixed Portions of the Dissolved Uranium for Cycles 1 and 2.

predicts that these phases appear in the above sequence during the dissolution of spent fuel and that the emergence of schoepite as a secondary solid phase causes a substantial increase in the uranium concentration. Because of an accelerated dissolution rate in the present experiment, the UO_2 powder may have reached a composition where the uranium concentration is being increasingly controlled by the schoepite, thereby yielding values similar to those predicted in the simulation study.

In addition to demonstrating the utility of MSID method in unraveling solid phase inhomogeneity problems, the experiment produced a great deal of information of interest to the forthcoming SFL leach tests.

1. The effectiveness of filters commonly used in leachate samplings was clarified. The failure of Nuclepore $0.4 \mu\text{m}$ filters to trap any suspended powder particles could have a similar effect on the fines in spent fuel. Filtrations with the Amicon cone membranes, on the other hand, appear to be too efficient, e.g., 31% of uranium is trapped from freshly prepared clear spiked solutions. A need for filtering media having intermediate pore sizes is indicated.
2. The uranium concentration in the leachate during cycle 1 goes through a maximum, eventually approaching a steady-state plateau. A similar effect has been observed in a previous SFL study [2], where such concentration peaks have been attributed to higher dissolution rates of hyperstoichiometric layers on the UO_2 matrix surface.
3. Replenishments with J-13 water of the sample volumes taken weekly for analysis required dilution corrections. Application of such corrections to SFL tests will be even more important because of larger leachate samples that will be needed for radionuclide analyses.
4. High rate of isotopic exchange reactions that will occur between the spiked leachate and specimen during cycle 2 of SFL tests will require an increased frequency of sampling. For this reason it is advisable to dedicate one SFL test for the singular purpose of monitoring the uranium isotope distribution by the MSID technique. As was done in the present experiment, such a test would allow taking an adequate number of small samples without a need for dilution corrections and to avoid mutual interferences with sampling procedures for other radionuclides.
5. The addition of a uranyl nitrate spike to J-13 water had no noticeable effect on the pH and ionic concentrations of the leachate, except for the expected increase in the NO_3^- concentration.
6. The experiment yielded high precision MSID data that would have been suitable for UO_x matrix dissolution rate measurements if the specimen were homogeneous. In that context, the feasibility of applying the MSID technique to spent fuel was established, but the validity of the kinetic model itself still remains to be demonstrated.

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REFERENCES

1. Site Characterization Plan, U.S. Department of Energy, Office of Civilian Radioactive Waste Management, DOE report DOE/RW-0198 (1988). HQO.881201.0001
2. C. N. Wilson, "Results from Cycles 1 and 2 of NNWSI Series 2 Spent Fuel Dissolution Tests," Hanford Engineering Development Laboratory report HEDL-TME 85-22 (1987). NNA.8707210.0058
3. C. J. Bruton and H. F. Shaw, "Geochemical Simulation of Reaction Between Spent Fuel Form and J-13 Water at 25 and 90°C," Mat. Res. Soc. Symp. Proc. Vol. 112, p. 485 (1988). NNA.891006.0182
4. L. Lynds, W. A. Young, J. S. Mchl, and G. G. Libowitz, in Nonstoichiometric Compounds, Advan. Chem. Ser. 39, R. F. Gould, ed., American Chemical Society, Chapter 5 (1962). NNA.900315.0296
5. H. G. Riella, L. G. Martinez, and K. Imakuma, "Determination of Crystallite Size in UO_{2+x} Powder by X-Ray Diffraction," J. Nucl. Mater. 153, 71 (1988). NNA.900312.0177
6. D. Vollath, in Gmelin Handbook of Inorganic Chemistry, Suppl. Vol. C4, Springer Verlag, Berlin, p. 20 (1984). NNA.900904.0244
7. J. F. Kerrisk, "Solubility Limits on Radionuclide Dissolution at a Yucca Mountain Repository," Los Alamos National Laboratory report LA-9995-MS, (1984). NNA.870519.0049
8. J. M. Delany, "Reaction of Topopah Spring Tuff with J-13 Water: A Geochemical Modeling Approach Using EQ3/5 Reaction Path Code," Lawrence Livermore National Laboratory report UCRL-53631 (1985). HQS.880517.2419
9. A. Hough and J. A. C. Marples, "Repository Source Term for Vitrified High Level Waste," Mat. Res. Soc. Symp. Proc. Vol. 127, p. 137 (1989). NNA.900315.0282
10. C. N. Wilson and C. J. Bruton, "Studies on Spent Fuel Dissolution Behavior Under Yucca Mountain Repository Conditions," presented at the American Chemical Society meeting, Indianapolis, IN, April 23-27, 1989, UCRL preprint 100223. NNA.900112.0111

APPENDIX A

This report does not use any information from the Reference Information Base nor contains any candidate information for the Reference Information Base or the Site and Engineering Properties Data Base (SEPDB).