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FROM SPENT NUCLEAR FUEL**

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L. D. Hafenrichter, and J. K. Bates

ARGONNE NATIONAL LABORATORY  
Chemical Technology Division  
9700 South Cass Avenue  
Argonne, IL 60439-4837

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## **COLLOIDAL PRODUCTS AND ACTINIDE SPECIES IN LEACHATE FROM SPENT NUCLEAR FUEL**

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Argonne National Laboratory, Chemical Technology Division, 9700 S. Cass Avenue, Argonne, IL 60439

### **SUMMARY**

Two well-characterized types of spent nuclear fuel (ATM-103 and ATM-106) were subjected to unsaturated leach tests with simulated groundwater at 90°C. The actinides present in the leachate were determined at the end of two successive periods of ~60 days and after an acid strip done at the end of the second period. Both colloidal and soluble actinide species were detected in the leachates which had pHs ranging from 4 to 7. The uranium phases identified in the colloids were schoepite and soddyite. In addition, the actinide release behavior of the two fuels appeared to be different for both the total amount of material released and the relative amount of each isotope released.

### **INTRODUCTION**

The volcanic tuff beds at Yucca Mountain, Nevada, are being investigated as the site of a repository for spent fuel and other high level waste. Information is needed to bound the potential radionuclide source term that would result within the repository and engineered barrier system after a fuel cladding failure. Since the Yucca Mountain repository will be in an unsaturated zone, cladding failure would expose the fuel to air in an unsaturated water environment. To simulate this environment, we have initiated ongoing unsaturated tests in which spent fuel is exposed to small, intermittent amounts of liquid groundwater (0.75 mL injected once every 3.5 days).

This paper will focus on the detection and identification of the colloidal species observed in the leachate that was collected after each

of the first two successive testing periods of approximately 60 days each. In addition, preliminary values for the total actinide release for these two periods are reported.

## **EXPERIMENTAL**

Two types of well-characterized spent fuel from pressurized water reactors were tested: ATM-103 with a burn-up of 30 MW-d/kg M [1] and ATM-106, with a burn-up of 43 MW-d/kg M [2]. The grain sizes were 9-19 [1] and 6-14 [2]  $\mu\text{m}$ . The fuel fragments (chunks weighing 0.3 to 1.2 g) had an average geometric surface area of 2.1  $\text{cm}^2/\text{g}$ . Prior to use, the fragments were dry-sieved on a 20-mesh sieve (840 nm) to remove fines. The tests on ATM-103 fuel were identified by the designation S32J1, and those on ATM-106 fuel by S62J1. (A number after the test designation indicates the length of the interval: for example, a leachate sample labeled S32J1-57 was removed after 57 days of testing.)

The groundwater originated from well J-13 and had a chemistry representative of the saturated zone below Yucca Mountain, Nevada. The water was equilibrated for 80 days at 90°C with crushed core samples of Topopah Spring tuff. The resulting water, designated EJ-13, had the following composition ( $\mu\text{g}/\text{mL}$ ): Al (0.68), B (0.19), Ca (6.95), K (6.67), Li (0.03), Mg (0.08), Na (53.6), Si (45.5),  $\text{NO}_3^-$  (10),  $\text{NO}_2^-$  (0.12),  $\text{SO}_4^{2-}$  (20), Cl (7.5), F (2.4), total carbon (25), organic carbon (5). The pH was 8.4.

The experiments were housed in stainless steel (type 304L) vessels. A small amount of EJ-13 water (5 mL) was initially deposited in the base of the vessel to ensure a humid atmosphere. The spent fuel was placed inside a Zircaloy-4 sample holder. The holder consisted of a 1.33-cm-diameter tube that was press-fitted into a 2.6 cm-square plate, which contained a 20- $\mu\text{m}$ -thick filter with 7- $\mu\text{m}$ -diameter holes. The fuel assembly was set on a ledge inside the test vessel and the vessel was

sealed (Fig. 1). The test vessels were held at 90°C in an oven. A small quantity of premeasured EJ-13 water (0.75 mL) was periodically dripped every 3.5 days from a reservoir onto the top of the spent fuel in the holder. Air was flushed through the lines to insure that the water left the lines and contacted the fuel (Fig. 2).

At two intervals of approximately 60 days, the two experiments were interrupted to collect the accumulated liquid and to visually examine the spent fuel samples. The volume of fluid present was determined by measuring the difference in vessel weight between the beginning and the end of each test interval. On average about 90-92% of the injected fluid was recovered. After disengaging the vessel from the injection system, it was rapidly cooled and then opened. The spent fuel assembly was removed from the vessel and examined visually (a video recording was retained). The assembly was then reintroduced into the same vessel after removal of the leachate or into a new test vessel if an acid strip of the vessel was to be done. If the same vessel was used, the assembly was kept in a moist environment while the leachate was removed from the test vessel.

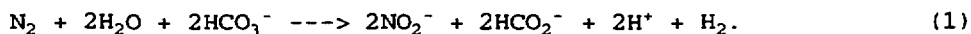
Aliquots of the leachate were taken and examined for pH (Brinkmann Metrohm Meter), carbon content (Dohrmann Total Carbon Analyzer), anion content (ion chromatography), radionuclide content in dissolved and suspended material (alpha spectroscopy of unfiltered and filtered leachate [3.6-nm filter, which was prewetted with deionized water]), radionuclide content (gamma spectroscopy), and elemental release (Fisons inductively coupled plasma-mass spectrometry [ICP-MS]). Suspended material was characterized using a JEOL 2000 FXII transmission electron microscope (TEM), operated at 200 kV and equipped with X-ray energy dispersive spectrometry (EDS) and parallel electron energy loss spectrometry (EELS). Electron diffraction data were compared to X-ray diffraction data to assist in identification of phases. The camera

lengths for selected area electron diffraction (SAED) were determined by using a polycrystalline aluminum sample. TEM samples were prepared by filtering a drop of leachate solution through a 'holey' carbon grid with holes of 100 nm [3].

Each test vessel was replaced at the end of the second test period. The used vessel was filled with 1% nitric acid (a mixture of Ultrex and deionized water) and heated at 90°C for 16 hours to remove any species that had adhered to the vessel walls. Aliquots of the acidified solution were then analyzed by gamma and alpha spectroscopy and ICP-MS. This procedure was designated as an acid strip.

## RESULTS

The pH of the four leachate samples was lower than that of EJ-13, (pH 8.4). For the test with ATM-103 fuel (S32J1), the leachate had a pH of 6.0 at 57 d and 6.3 at 120 d. For the test with ATM-106 fuel (S62J1), the leachate had a pH of 6.2 at 55 d and 4.7 at 113 d. For these four samples, the formate concentration, which was below detection limits for EJ-13, had increased to 6 and 9.2 x 10<sup>-3</sup> g/L for the S32J1 leachates (at 57 d and 120 d, respectively) and to 6.3 and 4.6 x 10<sup>-3</sup> g/L for the S62J1 leachates (at 55 d and 113 d, respectively). The change in the anion composition has been reported previously [4]. The major change noted was that the formate ion content increased in parallel with a decrease in bicarbonate and an increase in nitrite. A possible reaction, which summarizes this effect, is



Formate ion and higher order organics could combine with the actinides to form highly stable, soluble complexes which could increase the transport of actinide species [5].

## Quantification of Actinide Release

Table 1 shows the concentrations of the actinide species identified by alpha spectroscopy in unfiltered and filtered (3.6-nm filter) leachate samples. The amount of material which appears to be present as colloidal material is the difference in content between the unfiltered and the filtered leachate samples. For both leachates, this difference is >90%. Characterization of the colloidal material is addressed in a later section.

No actinide species were observed in either the filtered or the unfiltered leachate from the first test interval for the ATM-106 test. The peak at 5.5 MeV was assigned to americium-241 rather than plutonium-238 when americium-243 was detected and/or the correct plutonium-239/238 ratio was not found. Attenuation of the americium-241 peak may have obscured the presence of plutonium-239 and neptunium-237 in unfiltered aliquots, especially if they were observed in a filtered aliquot. For the ATM-103 test, the amount of americium present in the filtered leachate is orders of magnitude greater than that found in saturated tests, in which a 1.3-nm filter [6] was used in place of our 3.6-nm filter.

Tables 2 and 3 show the actinide and cesium content in the two successive leachate samples and in the acid strip, as measured by alpha, and gamma analyses and preliminary semi-quantitative ICP-MS results, for the ATM-106 and ATM-103 tests, respectively. The semi-quantitative ICP-MS values agreed within an order of magnitude with the gamma values. Therefore, since ICP-MS results were available for most isotopes, we used these values to compare the relative release of all actinides for the two different tests. This comparison is found in Table 4. In addition, we have included in Table 4 the fraction of maximum material release for each actinide during the two test intervals. The maximum material release is the total quantity of a given isotope in the spent fuel

sample. Last, we calculated for each isotope the ratio between the amount of material detected in the leachate versus the total in the base of the test vessel which included that adhered to the stainless steel vessel wall. This latter ratio was labeled soluble fraction in that this represents the material which had not deposited on the vessel walls. This soluble fraction includes however, both colloidal material and ionic material.

The information in Table 4 is the basis of the following observations for the ATM-106 fuel. First, during the first test period only a minor actinide release was detected in the ATM-106 leachate. Second, the fraction of maximum actinide released was ten times greater than the fraction of maximum uranium released. Third, for the ATM-106 fuel, most of the actinides (columns 3-6 of Table 4) which were released appeared to be deposited on the walls of the stainless steel vessel (the latter is labeled acid strip). Cm-244 appeared to be the one actinide with a large soluble fraction (0.23).

For the ATM-103 fuel, the major actinide release appeared to have occurred in the first test period. Second, the fraction of maximum actinide released was not the same for all actinides. The fraction for plutonium and uranium were equivalent ( $1 \times 10^{-5}$ ) but were three orders of magnitude smaller than the fraction for americium and curium ( $1 \times 10^{-2}$ ). Third, the soluble actinide fraction was high for ATM-103 fuel ranging from 0.44 to 0.88.

There was an additional difference between the two fuels. If one uses the fraction of maximum uranium release as a basis of comparison, half as much material was released from the ATM-106 fuel over the two test periods as that from the ATM-103 fuel. Because the two fuels had different burn-up histories, this may have had an influence on their release behavior. Results from additional test intervals will be needed to determine if these differences in the two fuels persist.

## Characterization of Colloidal Material

Identification of the colloidal material in the leachate was done using transmission electron microscopy. The phases identified are shown in Table 5. Non-uranium-bearing phases which were mainly calcium and silicon-bearing particles were commonly found. The TEM sample from leachate S32J1-57 (ATM-103 fuel) contained two major, intermixed uranium phases which contained rare earth elements (REEs). The uranium to silicon ratio in these two phases appeared to vary. Partially crystalline uranium silicate colloids were identified by SAED analysis and EDS compositional data, as soddyite, a uranyl silicate with a U/Si ratio of 1:1. The individual particles were 50-100 nm in diameter. A micrograph of the agglomerated colloid is shown in Fig. 3, as is the SAED analysis which suggested that this phase was soddyite. The EDS of the uranium soddyite phase is shown in Fig. 4a.

The second uranium-bearing phase which consisted of 20-50 nm particles in agglomerates, which were 3-5  $\mu\text{m}$  in diameter, contained very little silicon but a small amount of a mixture of REEs. The phase was not crystalline, however, the elemental composition suggested a schoepite phase (a uranyl hydrate species). The EDS of this phase is shown in Fig. 4b. A second difference technique was used with EELS, which has a higher detection sensitivity than EDS, to confirm the identity of the REEs. (This technique takes the difference of three spectra at increasing energy offset to remove the channel-to-channel gain variation [7].) A micrograph of the agglomerate is shown in Fig. 5a. The identified REEs are shown in Fig. 5b (La, Ce, Pr, Nd, Sm, and Eu). The REEs are fission products which are present in the spent fuel samples.

The uranium phases found in these leachate tests form part of the paragenic sequence found for unirradiated  $\text{UO}_2$  dissolution [8]. The presence of both schoepite and soddyite appears to indicate that the uranium in the spent fuel matrix is dissolving in a manner similar to



that found for unirradiated  $\text{UO}_2$ . However, the actinides in the spent fuel do not appear to be released congruently with the uranium matrix.

## CONCLUSIONS

Uranium and actinide release from two spent fuel samples under unsaturated conditions appeared to depend on the fuel characteristics. This seemed to hold both for the total amount of material released and the relative amount of each isotope released compared to the uranium release. In addition, for the ATM-103 fuel, a large fraction of the actinides released was in the form of colloids. Two species identified in these colloids were schoepite and soddyite, phases identified as part of the paragenic sequence of  $\text{UO}_2$  dissolution.

## ACKNOWLEDGMENTS

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**Table 1. Actinide Species (g/L) Detected by Alpha Spectroscopy for Successive Unfiltered and Filtered Leachate Samples**

Fuel	Test No. <sup>a</sup>	Content of Unfiltered Sample				
		Cm-244	Am-241	Am-243	Pu-239	Np-237
ATM-103	S32J1-57	4.9E-6	3.6E-5	8.5E-6	ND <sup>b</sup>	ND
ATM-103	S32J1-120	2.0E-6	1.3E-5	ND	ND	ND
ATM-106	S62J1-55	ND	ND	ND	ND	ND
ATM-106	S62J1-113	4.1E-8	2.1E-7	3.4E-7	ND	ND
Fuel	Test No. <sup>a</sup>	Content of Filtered Sample				
		Cm-244	Am-241	Am-243	Pu-239	Np-237
ATM-103	S32J1-57	1.7E-7	1.2E-6	6.4E-8	4.5E-7	1.1E-4
ATM-103	S32J1-120	2.1E-7	9.1E-7	4.8E-8	2.9E-7	2.2E-5
ATM-106	S62J1-55	ND	ND	ND	ND	ND
ATM-105	S62J1-113	4.7E-9	4.5E-9	ND	ND	ND

<sup>a</sup>Number following hyphen is test time in days when aliquot was taken.

<sup>b</sup>ND = No species were detected.

Table 2. ATM-106 Test - Actinide and Cesium Content<sup>a</sup> (g/L)  
for the Leachate and the Acid Strip (Gamma, Alpha, and  
ICP-MS Analyses)

	U-238	Pu-239	Am-241	Am-243	Cm-244	Cs-137
Leachate, 1st 60 d						
Alpha	NA	ND	ND	ND	ND	NA
Gamma	NA	NA	ND	ND	NA	2E-8
ICP-MS	7E-8	1E-9	5E-10	1E-9	1E-9	2E-7
Leachate, 2nd 60 d						
Alpha	NA	ND	2E-7	3E-7	4E-8	NA
Gamma	NA	NA	ND	9E-6	NA	2E-6
ICP-MS	4E-4	1E-6	8E-7	3E-7	3E-7	8E-5
Acid Strip						
Alpha	NA	1E-5	<1E-6	ND	3E-7	NA
Gamma	NA	NA	1E-6	2E-7	NA	5E-6
ICP-MS	9E-4	6E-6	2E-6	6E-7	2E-7	8E-6

<sup>a</sup>The symbol ND is used if the species was not detected, and NA if a technique was not applicable.

**Table 3. ATM-103 Test - Actinide and Cesium Content<sup>a</sup> (g/L)  
for the Leachate and the Acid Strip (Gamma, Alpha, and  
ICP-MS Analyses)**

	U-238	Pu-239	Am-241	Am-243	Cm-244	Cs-137
Leachate, 1st 60 d						
Alpha	NA	4E-7 <sup>b</sup>	4E-5	6E-8 <sup>b</sup>	5E-6	NA
Gamma	NA	NA	3E-4	1E-4	NA	2E-4
ICP-MS	4E-3	1E-6	2E-4	4E-5	6E-5	8E-5
Leachate, 2nd 60 d						
Alpha	NA	3E-7 <sup>b</sup>	1E-5	5E-8 <sup>b</sup>	2E-6	NA
Gamma	NA	NA	1E-5	5E-4	NA	3E-4
ICP-MS	1E-3	5E-7	2E-5	3E-6	2E-6	2E-4
Acid Strip						
Alpha	NA	ND	2E-5	ND	1E-6	NA
Gamma	NA	NA	2E-5	4E-6	NA	8E-7
ICP-MS	8E-4	4E-7	2E-5	5E-6	2E-6	2E-6

<sup>a</sup>The symbol ND is used if the species was not detected, and NA if a technique was not applicable.

<sup>b</sup>The amount detected for the filtered aliquot.

**Table 4. ATM-106 and ATM-103 Tests - Actinide and Cesium Content<sup>a</sup> (g), Fraction Released and Soluble Fraction**

	Fuel Type: ATM-106					
	U-238	Pu-239	Am-241	Am-243	Cm-244	Cs-137
Leachate 1st 60 d	7E-10	1E-11	5E-12	1E-11	1E-11	2E-9
Leachate 2nd 60 d	4E-6	1E-8	9E-9	3E-9	3E-9	9E-7
Acid Strip	5E-5	3E-7	1E-7	3E-8	1E-8	5E-7
Total	5E-5 <sup>b</sup>	3E-7	1E-7	3E-8	1E-8	1E-6
Soluble Fract. <sup>c</sup>	0.07	0.03	0.09	0.09	0.23	0.64
Fract. of Maximum <sup>d</sup>	8E-6	6E-5	1E-4	1E-4	2E-4	1E-3
	Fuel Type: ATM-103					
	U-238	Pu-239	Am-241	Am-243	Cm-244	Cs-137
Leachate 1st 60 d	4E-5	1E-8	2E-6	4E-7	7E-7	9E-7
Leachate 2nd 60 d	1E-5	6E-9	2E-7	4E-8	2E-8	2E-6
Acid Strip	5E-5	2E-8	1E-6	3E-7	1E-7	1E-7
Total	1E-4 <sup>b</sup>	4E-8	3E-6	7E-7	8E-7	3E-6
Soluble Fract. <sup>c</sup>	0.50	0.44	0.69	0.59	0.88	0.97
Fract. of Maximum <sup>d</sup>	1E-5	7E-6	6E-3	9E-3	6E-2	4E-3

<sup>a</sup>Values are derived from semi-quantitative ICP-MS results.

<sup>b</sup>The uranium release corresponds to 0.26 mg/m<sup>2</sup>-d for ATM-106 and 0.46 mg/m<sup>2</sup>-d for ATM-103. (This is for an estimated average surface area.)

<sup>c</sup>The fraction of isotope present in the leachate and not deposited on the vessel walls.

<sup>d</sup>The fraction of the maximum amount of isotope present in the spent fuel sample.

**Table 5. Characterization of Colloids by Transmission Electron Microscopy**

Sample <sup>a</sup>	Phases	Comments	Elements
Leachate, 1st 60 d			
S62J1-55	Aluminum particles	Agglomerated	Al
S32J1-57	Schoepite hydrate	Individ. 20-50 nm	U, REE <sup>b</sup>
	Soddyite	Individ. 50-100 nm	U, Si, REE
	Calcium silicate	---	Ca, Si
Leachate, 2nd 60 d			
S62J1-113	Calcium phases	Particles, agglom.	Ca, Zn
S32J1-120	Silica	---	Si

<sup>a</sup>Number following hyphen indicates time in days at which leachate was taken.

<sup>b</sup>REE = rare earth elements.

## FIGURE CAPTIONS

- Figure 1. Assembled test vessel, liquid at base is not shown.
- Figure 2. Water injection system.
- Figure 3a. Micrograph of agglomerated colloid; individual particles were 50-100 nm in diameter.
- Figure 3b. SAED of colloid which suggested phase was soddyite.
- Figure 4a. EDS of uranium soddyite phase.
- Figure 4b. EDS of uranium only phase.
- Figure 5a. Micrograph of uranium only phase; dark areas were location of REEs.
- Figure 5b. Second difference EELS of uranium phase; REEs identified.



FIGURE 1

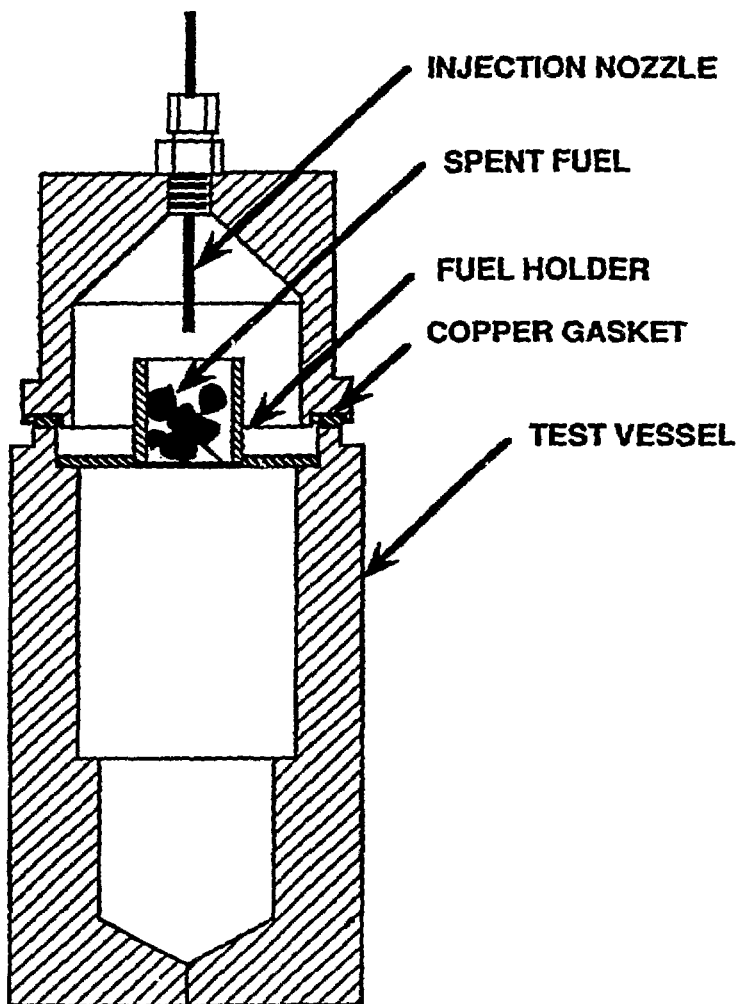


FIGURE 2

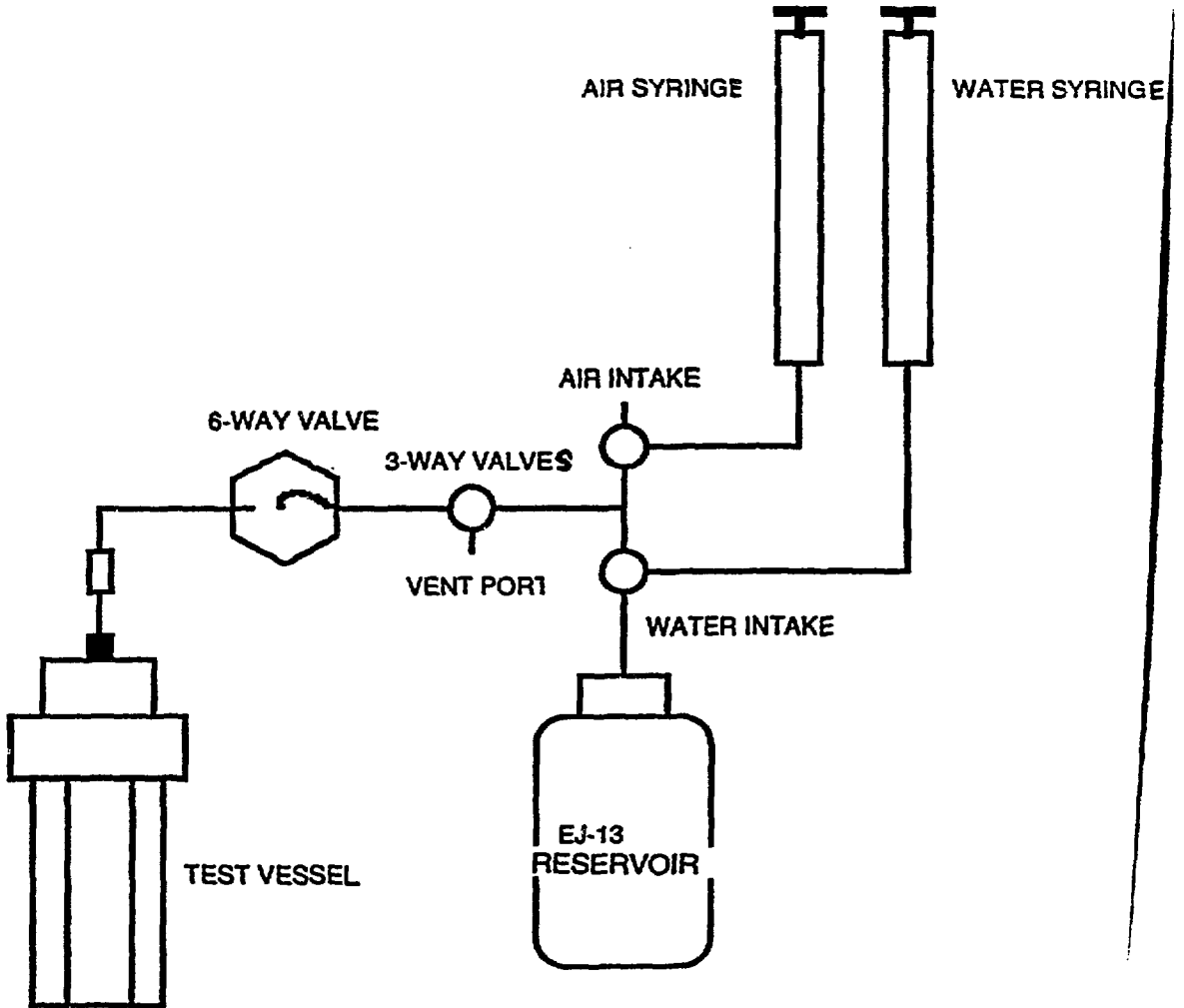


FIGURE 3a



FIGURE 3b

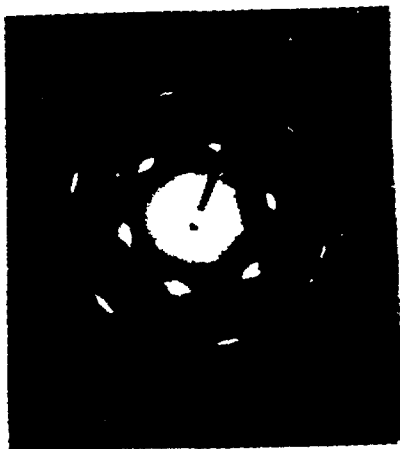


FIGURE 4a

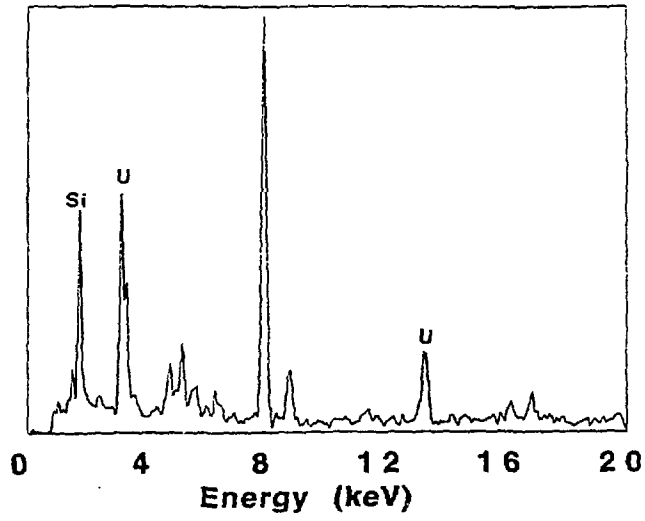


FIGURE 4b

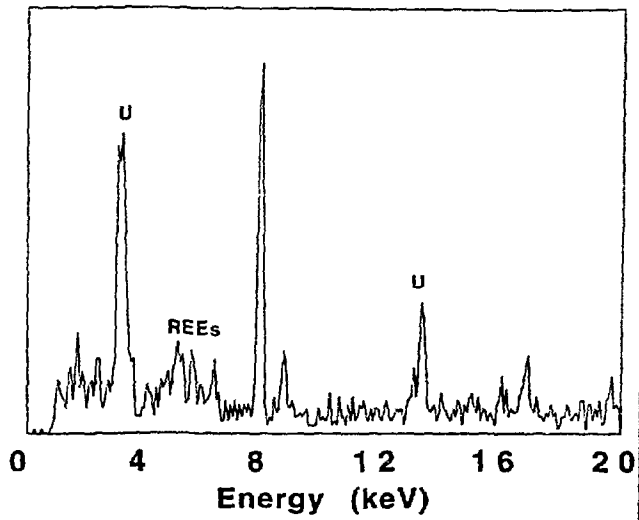


FIGURE 5a

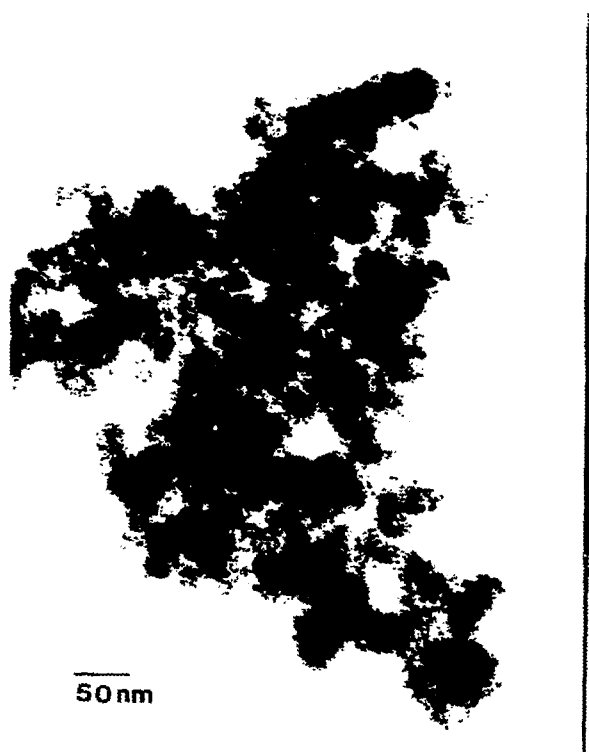


FIGURE 5b

