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## IDENTIFICATION OF COLLOIDS IN NUCLEAR WASTE GLASS REACTIONS

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### ABSTRACT

Characterization data for particulates formed under a variety of laboratory leaching conditions that simulate glass reaction in a repository environment are presented. Data on the particle size distributions and filterable fractions for neptunium, plutonium, americium, and curium were obtained by filtration through a series of filters with pore sizes ranging from 1  $\mu\text{m}$  to 3.8  $\mu\text{m}$ . The neptunium was found to be largely nonfilterable. Americium and plutonium were associated with filterable particles. The particles with which the americium, plutonium, and curium were associated were characterized using transmission electron microscopy (TEM) examination techniques.

### 1. INTRODUCTION

It is well known that colloidal particles are mobile in subsurface environments and can play an important role in the transport of contaminants.<sup>(1)</sup> However, the importance of colloids in assessing the radionuclide release performance of the engineered and natural barriers for the geologic disposal of high-level radioactive waste is not well established. While the role of colloid formation and transport in the release of radionuclides has been discussed in the literature,<sup>(2,3)</sup> there is little experimental information on the formation and characteristics of colloids formed in repository-relevant glass testing. Current performance assessment calculations assume that the mobile concentrations of most sparingly soluble radioelements in any groundwater that contacts the waste will be "solubility limited."<sup>(4,5)</sup> An important implicit assumption in this solubility-limited approach is that colloids are not formed or play an insignificant role in radionuclide release.

This paper is intended to examine the formation and characteristics of colloidal particles under a variety of waste glass testing conditions that are relevant to the candidate Yucca Mountain repository. It provides an initial basis for evaluating the need to consider the role of colloids in transporting radionuclides out of the waste packages and the repository engineered barrier system.

## 2. EXPERIMENTAL

The experimental results that are discussed in Section 3 were obtained by filtration of leachates, from a variety of waste glass tests, through a sequence of membrane filters with pore sizes ranging from 5  $\mu\text{m}$  to 2.8 nm. The filterable and nonfilterable fractions for Np-237, Pu-239, Pu-238, Am-241, and Cm-244 in the leachate were determined using alpha spectroscopy. In addition, the particles that were isolated by wicking small leachate droplets through a holey carbon grid were examined using the TEM. An outline of the types of waste glass that were tested, the test conditions, and the ultrafiltration and counting methods that were utilized follows.

### 2.1 The Waste Glass Characteristics and Testing Conditions

A variety of waste glasses, designated ATM-8, 131/11, 165/42, 200R, and 202A were utilized. These designations are based mainly on a range of Savannah River Laboratory (SRL) waste glass composition recipes<sup>(6)</sup> and are described below:

- the 165/42 glass denotes a composition based on the 165 type frit and sludge from tank 42. It represents the glass durability target that was used during frit development at SRL;
- the 131/11 glass denotes a composition based on the 131 type frit and sludge from tank 11. It represents a lower bound on the acceptable durability range;
- the 200R glass denotes a composition based on the 200 type frit and sludge from tanks 8 and 12 with a nonradioactive analog additive for the PHA feed;
- the 202A glass denotes a composition based on the Defense Waste Processing Facility (DWPF) startup frit with additions to make it similar to the target glass that is identified in the Waste Compliance Plan for the initial DWPF production campaigns;
- the ATM-8 glass is a reference glass composition documented in reference 7. It is not a DWPF-based glass.

Samples of these glasses in the form of monolithic disks or crushed (sieve size 100-200 mesh) powders were leached in J-13 well water under the matrix of test conditions shown in Table 1. Each leach test was performed in conventional 304L stainless steel Parr vessels which were sealed using a copper compression gasket and kept, for the test duration, in a thermostatically controlled oven. At the end of each test, approximately 2 mL of the leachate was removed, weighed, and set aside for filtration purposes.

Table 1. Matrix of Test Conditions<sup>\*</sup>

Test Number	Glass Type/Form	SA/V (m <sup>-1</sup> )	Test Duration (d)
DP16	131/11-powder	2000	280
DP61 <sup>**</sup>	165/42-powder	2000	280
DP62 <sup>**</sup>	165/42-powder	2000	280
DP122 <sup>**</sup>	200R-powder	2000	14
DP123 <sup>**</sup>	200R-powder	2000	14
DP158	200R-powder	2000	14
PY11 <sup>**</sup>	131A-powder	2000	140
PY12 <sup>**</sup>	131A-powder	2000	140
BY11	202A-powder	2000	140
G523	ATM-8-disk	30	1460
G537 <sup>***</sup>	ATM-8-disk	30	1460

<sup>\*</sup>All tests were conducted at 90°C.

<sup>\*\*</sup>Duplicate tests.

<sup>\*\*\*</sup>Test similar to G523 with tuff disk included.

## 2.2 Ultrafiltration and Counting Methods

The leachate sample from each test was filtered sequentially through a series of Nuclepore<sup>®</sup> (polycarbonate) and Amicon Diaflo<sup>®</sup> (YM-cellulose) filters. In general, the filter pore size sequence utilized was 5, 1, 0.1, and 0.015  $\mu\text{m}$  Nuclepore<sup>®</sup> and Amicon YM 30 (pore size of approximately 3.8 nm). For filtration the filters were placed and sealed in a Gelmann filter housing. The leachate solution was forced through the filters by using a syringe to supply the leachate and the necessary filtration overpressure. After filtration, the amount of filtrate collected was weighed and an aliquot was deposited and dried on a stainless steel planchette for alpha counting. Also, the filters were removed from the filter housing and mounted on steel planchettes in a configuration suitable for alpha counting.

The filters and filtrate aliquots were counted using a calibrated Ortec model 576 alpha spectroscopy system. The observed count rates for the alpha peaks characteristic of Np-237, Pu-239, Pu-238, Am-241, and Cm-244, were used to calculate the filterable and nonfilterable concentrations for each isotope.

Samples, suitable for TEM examination, were prepared from selected leachate solutions by carefully wicking a small droplet of the leachate through a holey carbon TEM grid.

### 3. RESULTS

As mentioned in Section 2, alpha spectroscopy counting data were used to calculate the percentages of the leachate concentrations that were filterable (i.e., removed by the filter) and nonfilterable (i.e., transmitted by the filter) at each filtration step. The results obtained are shown in Table 2. The nonfilterable fractions are based on the alpha spectroscopy data for the filtrate aliquots that were collected after each filtration step. Data for the percent filtered were obtained, by difference, from the concentration in the solution that was filtered and the filtrate concentration. The Pu results for the DP-16 test are discussed here to illustrate how the Table 2 data should be interpreted. For this test, 4% of the Pu leachate concentration was removed (i.e., filterable) by the 5  $\mu\text{m}$  filter, 7% by the 1  $\mu\text{m}$  filter, 80% by the 0.1  $\mu\text{m}$  filter, and 3 and 4% respectively by the 0.015 and 0.0038  $\mu\text{m}$  filters. Only 2% of the original Pu concentration remained in the solution (i.e., was nonfilterable) after the 0.0038  $\mu\text{m}$  filtration stage. This corresponds to a Pu concentration of  $2.5\text{E-}12$  moles/liter.

The alpha spectroscopy data obtained by counting filters was used to check for closure of the mass balance after each filtration step. The filter and filtrate data were generally consistent with mass balance closure. However, in some cases, particularly when the filtrate data indicated that significant fractions (>20%) were filterable by the Amicon YM 30 filters, mass balance closure was not achieved. We believe that this may be due to trapping of the particles within the membrane which results in counting errors due to attenuation or stopping of some of the alpha particles in the filter.

Figure 1 shows a brightfield electron micrographs of particles that were collected on a TEM grid for the DP-158 test (see Table 2). These micrographs were obtained using a 200 keV analytical electron microscope. The larger particle shown in Figure 1b is believed to be a piece of the reacted layer that has spalled from the glass surface. The particles shown in Figure 1a are believed to be typical of those that account for the filtration results presented here. They range in size from about 2000 Å to less than 100 Å. The elemental composition of these particles is mostly sodium, potassium, aluminum, and silicon. Because they are amorphous, the phases involved could not be identified.

The residual concentrations in the filtrate solution after passage through the last filter in the filtration series provides an indication of the true solution concentrations. These data are tabulated in Table 2.

### 4. DISCUSSION AND CONCLUSIONS

The results presented here were obtained through an initial scoping study for which the objective was to provide an overview of how colloidal particles, formed under a variety of repository-relevant test conditions, influence the total concentrations of actinide elements in leach solutions. Many potentially important issues, such as the effects of temperature changes and leachate storage on the colloidal particles, remain to be investigated.

Table 2. Results for Filtration Series

Test Number	Filter Pore Size ( $\mu\text{m}$ )	Nonfilterable Fraction (%) <sup>*</sup>				Filterable Fraction, (%) <sup>*</sup>			
		Np	Pu	Am	Cm	Np	Pu	Am	Cm
DP16	5.0		96		89		4		1
	1.0		89		99		7		-
	0.1		9		14		80		85
	0.015		6		10		3		4
	0.0038		(2.5E-12)		(3.5E-15)		4		6
DP61/62 <sup>***</sup>	1.0		102		100		0		0
	0.1		83		80		19		20
	0.05		80		77		3		3
	0.015		80		77		0		0
	0.0038		(5.7E-11) <sup>**</sup>		(1.9E-13) <sup>**</sup>		70		70
DP122/123 <sup>***</sup>	5.0		115		100		0		0
	1.0		103		78		0		22
	0.1		91		59		12		19
	0.0038		(4.6E-11)		(9.4E-13)		65		40
			26		19				
DP158	5.0		100	100		0	0		
	1.0		119	138		0	0		
	0.1		62	65		57	73		

Cont'd

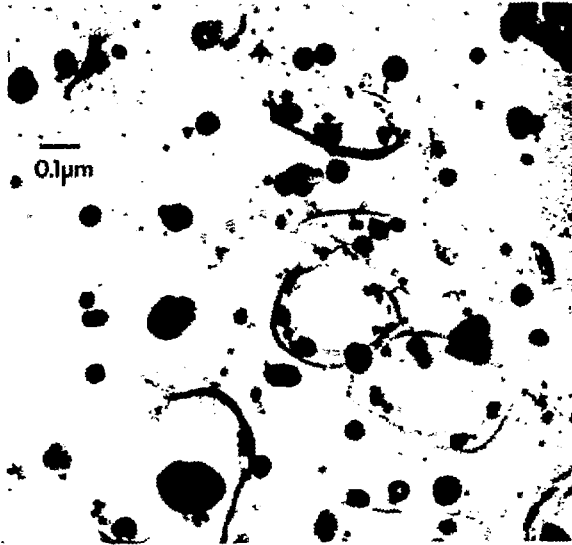
Table 2 (Cont'd)

Test Number	Filter Pore Size ( $\mu\text{m}$ )	Nonfilterable Fraction (%) <sup>*</sup>				Filterable Fraction, (%) <sup>*</sup>			
		Np	Pu	Am	Cm	Np	Pu	Am	Cm
G523	5.0	86	87			14	13		
	1.0	90	21			0	66		
	0.1	85	15			1	6		
	0.0038	(4.9E-7) 85	(1.0E-10) 11			0	4		
G537	5.0	103	110			0	0		
	1.0	112	75			0	35		
	0.1	112	48			0	27		
	0.0038	(1.1E-6) 92	(2.6E-10) 10			8	38		
PY11/12 <sup>***</sup>	5.0		100	100			0	0	
	1.0		88	94			12	6	
	0.1		37	27			51	67	
	0.0038		(1.1E-9) 12	(7.3E-12) 7			25	20	
BY11	5.0		101	89			0	11	
	1.0		80	77			21	12	
	0.1		62	75			18	2	
	0.0038		(7.6E-9) 20	(1.4E-10) 14			42	51	

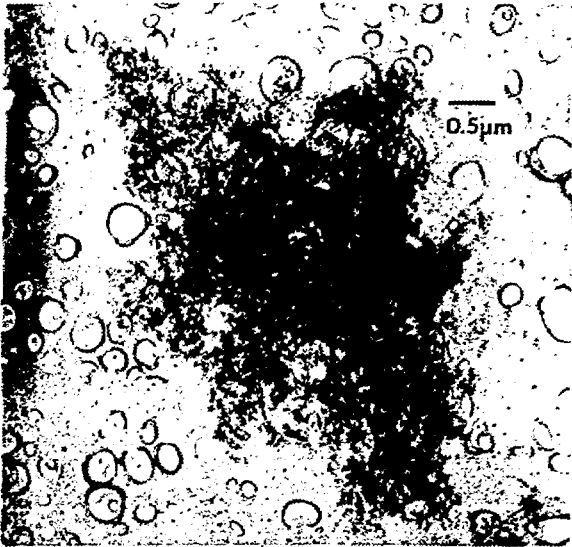
<sup>\*</sup>The filterable and nonfilterable fractions are shown as percentages of the concentration in the leachate.

<sup>\*\*</sup>The numbers in parentheses are the corresponding nonfilterable concentrations expressed as moles/liter.

<sup>\*\*\*</sup>Average data from duplicate tests.



(a)



(b)

Figure 1. TEM Micrographs of Particulate Material Isolated on a Holey Carbon TEM Grid



The data for Np (see the results for the G523 and G537 tests in Table 2) indicate that less than 15% of the solution concentration is filterable even at the 3.8 nm filter pore size. This result is consistent with Np results reported previously.<sup>(8)</sup> In contrast to Pu, Am, and Cm, the Np data are consistent with the expectation that the concentration is dominated by the material in true solution and that colloidal formation and transport may not play an important role in Np release from the waste packages and EBS.

Most (up to 100%) of the Pu, Am, and Cm concentration in glass leachate solutions is associated with particulate material in the colloidal size range. The size distribution (as indicated in Table 2 by the fractions that are filterable by the different pore size filters) changes significantly from test to test. The size distributions are probably influenced by a broad range of factors, including glass type, test duration, and test conditions, which are not well understood at this point. However, the fractions of these elements (i.e., Pu, Am, Cm) associated with the different size fractions do not appear to be element specific. Where data are available for more than one of these elements they appear to follow the same trend.

Although the work reported here is in an early scoping phase, the results indicate that the performance assessment assumption that groundwater concentrations of actinide elements will be solubility limited should be reexamined. This conclusion applies particularly to modeling the release of Pu, Am, and Cm isotopes from waste packages containing nuclear waste glass.

## 5. ACKNOWLEDGMENTS

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