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GEOCHEMICAL ASSESSMENT OF NUCLEAR WASTE ISOLATION

R.J. Silva, and A.W. Yee

April 1982

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GEOCHEMICAL ASSESSMENT OF NUCLEAR WASTE ISOLATION

TOPICAL REPORT

Testing of Methods for the Separation of Solid and Aqueous Phases

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ABSTRACT

Measurement of the solubilities of certain waste radionuclide compounds will be necessary to adequately assess and predict the ability of potential underground waste storage facilities to meet federally established performance criteria. During such measurements, it is usually necessary to physically separate solid and solution phases. Experiments have been conducted to test and compare the relative efficacy of three commonly used separation methods, i.e. gravity settling, centrifugation and filtration. The results indicated that sorption of solution species onto filters can occur and could potentially lead to erroneous results in solubility measurements when one is dealing with trace amounts of radionuclides in solution. The degree of retention by filters depended on the solution pH and the nature of the filter material. Of the three methods, centrifugation appeared to give the most reliable and consistent results. Filtration was found to give results comparable to centrifugation if care is taken in the selection of filter type.

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1.0 INTRODUCTION

1.1 Background

Moving groundwater is expected to provide the mechanism by which nuclear waste could be transported from an underground storage facility to the accessible environment (1). In order to predict the rates of radionuclide migration, knowledge of the processes which control residence times of radionuclides in the aqueous and solid phases is needed.

In the event that the canister and waste form fail to contain radioactive waste materials, radionuclides will enter the local groundwater system. The radionuclides will react with various components of the groundwater, and possibly the host rock, to form insoluble compounds and solution species which can provide major controls on the solution concentrations and migration rates of the radionuclides. Precipitation of stable solid phases will retard the migration of radionuclides relative to the average velocity of groundwater; on the other hand, formation of aqueous complexes will tend to reduce this retardation effect. Thus, knowledge of the solubility of compounds can provide the first step in the assessment of amounts and rates of release of radionuclides from an underground facility. Therefore, thermochemical data on the solubilities of compounds of the waste radionuclides likely to form in the natural systems are required to adequately assess and predict the ability of the storage site to meet established site characteristics and standards for rates of release of radioactive materials set by the Nuclear Regulatory Commission in 10 CFR 60 (2) and 40 CFR 191 (3). To obtain this information, it may be necessary to identify precipitates that form under the groundwater conditions and to measure their solubilities.

Measurement of the solubility of a compound in aqueous solution involves basically the following steps: formation or preparation of the solid under equilibrium conditions, solid phase characterization, separation of the solid and aqueous phases, and analysis of the aqueous phase for the dissolved species (4). Although this appears to be a straightforward procedure, a number of problems can arise that can cast doubt on the reliability of the measurement. Unfortunately, many of the experiments reported in the literature fall into this category due to failure to carry out all the steps or failure to demonstrate the effectiveness of a step. Therefore, current methods and techniques for measuring solubilities should be assessed and tested as to their accuracies and potential inadequacies so as to establish reliable, standarized methods. This report covers tests on the methods for the separation of solid and aqueous phases in solubility measurements. This information is pertinent to the establishment of reliable procedures for conducting solubility measurements on waste radionuclides.

The issue of the solubility of radionuclides is related to the following sections of 10 CFR Part 60: 60.11 (a); 60.21 (c) (1), (3); 60.31 (a) (1) (i); 60.111 (b) (1), (2) (ii), (3); 60.122 (d), (g) (1), (2); 60.123 (a) (8), (b) (13), (14) (15); 60.132 (a) (2).

2.0 SEPARATION OF SOLID AND AQUEOUS PHASES

2.1 Statement of Problem

The compounds of many of the long-lived waste radionuclides that are likely to form in natural systems are very insoluble and very low solution concentrations of the radionuclides would be expected, e.g., 10^{-8} to 10^{-12} M. A number of papers have appeared in the literature concerning the formation of psuedocolloids and other sorption phenomenon exhibited by trace amounts of radionuclides in nearly neutral pH solutions (5, 6, 7, 8) that can lead to erroneous solubility determinations. Pseudocolloids can form when species in solution are sorbed on particles of colloidal size, e.g. silica (5, 8).

The technique employed for separating the solution from the solid phase in solubility studies is usually described only briefly, and frequently not at all, in the published literature. Often the solid phase is simply allowed to settle for an extended period of time before an aliquot of the aqueous phase is withdrawn for analysis. This method could allow suspended or colloidal material to be withdrawn as well. Another common method is centrifugation. However, rarely is a discussion given of the minimum time or revolution speed (precipitating force) needed to achieve adequate separation or is a verification of the effectiveness of the separation made. Finally, filtration is often used as a final or single separation step. Few reported studies indicate that the effects of pore size or filter material had been examined. However, the use of two or three decreasing pore size filters, e.g., in the range of 0.4 to 0.015 micrometer, to filter the same samples is becoming popular. If the measured concentration

of the solution component is constant for the different pore sizes, it is taken as verification of effective separation. There is some evidence that the filters themselves may at times adsorb soluble species from solution and that different materials and different filter constructions behave differently in this respect (9); however, no systematic studies have been reported.

2.2. Experimental Measurements and Results

2.2.1 Preliminary Experiments with UO_2^{2+}.

Preliminary experiments were conducted to determine if sorption of solution species by components of the two most popular separation methods, i.e., centrifugation and filtration, could influence solution concentrations.

When measurements were to be isolated from air, a model HE-43-2 inert atmosphere box obtained from Vacuum Atmospheres Company of Hawthorne, California was used. The pH measurements were made with a Beckman model 9505 micro-combination glass electrode coupled to an Orion model 399A pH meter. Centrifugations were made with an Eppendorf (Brinkmann) model 5412 microcentrifuge obtained from Scientific Products of Sunnyvale, California. Filters were of two types: (1) polysulfone acrodics from Gelman, Ann Arbor, Michigan and (2) polycarbonate films from Nuclepore Company, Pleasanton, California. The liquid samples were alpha counted with a microprocessor controlled liquid scintillation counter model 460C obtained from Packard Instrument Company, Downers Grove, Illnois. The ultrapure HCl, NaOH and NaCl used in preparing solutions were obtained from Alpha Division of Ventron Corporation of Danvers, Massachusetts.

Duplicate samples containing 50 ml of 10^{-6} M $^{233}UO_2^{2+}$ were prepared in Nalgene linear polyethylene bottles with 0.01 M NaCl as supporting electrolyte. The ^{233}U used was first purified and the hexavalent ions separated by selective elution from a Dowex 50 x 4 cation exchange resin column using various HCl concentrations as elutants (10). Distilled-deionized water was boiled for 30 minutes, cooled rapidly in an ice bath and flushed with argon for 15 minutes to remove dissolved CO_2. This water was then transferred to an inert atmosphere box (argon atmosphere) and the ^{233}U solutions prepared with this water and ultrapure NaCl. All subsequent experimental work was carried out in the inert box to exclude CO_2. The pH of the duplicate UO_2^{2+} solutions were adjusted to 8.0 ± 0.1 with ultrapure NaOH. The solutions were allowed to stand for up to 7 days with occasional stirring. The pH of each was checked daily and any adjustments necessary to maintain a pH of 8 were made. After 4 hours, 24 hours and 7 days, the bottles were agitated and aliquots were removed for centrifugation and filtration. About 1.25 mls of solution were centrifuged at 15,000 rpm for 10 minutes in an Eppendorf microcentrifuge. For our system, this should precipitate particles of approximately 0.1 μm diameter (11). One ml of the supernate was mixed with 10 mls of Packard insta-gel scintillation "cocktail" and gross alpha counted in a Packard liquid scintillation counter. A volume of 3 ml was filtered through 0.2 μm pore size acrodisc (polysulfone) disposal filters and an equal amount filtered through 0.015 μm pore size nuclepore (polycarbonate) filters. The first ml through the filters was discarded and 1 ml of the remaining filtrate taken for liquid scintillation counting. The final ^{233}U solution concentrations were calculated from the measured alpha counts.

The results of the centrifugation and filtration measurements are summarized in Table 2.1. Presented in the tables are the ratios of the concentrations of U in the separated samples to the concentrations of U originally made up in the nalgene bottles (referred to as fractions in the tables). All separations were carried out in duplicate.

For the solutions of 10^{-6} M in U, precipitation of uranyl hydroxide was not expected to occur on the basis of calculations using available thermochemical data (12). A high fraction of the initial U in the nalgene bottles (10-15% was absorbed on the bottle walls) appeared in the centrifuged and 0.2 μm filtered samples and the reproducibility was good (generally less than 5% variations). However, for the 0.015 μm filtered samples, substantial amounts of U were lost from solution. Since large fractions of U were apparently transferred from the bottles in the centrifuged and 0.2 μm filtered samplings, presumably the same was true for the 0.015 μm filtered samplings but the U was lost by sorption on the 0.015 μm filters, e.g., 40-50% loss. Reproducibility was also poor for these samples.

2.2.2 Testing of Different Filter Types

Since the preliminary experiments with UO_2^{2+} indicated that the nature of filters used in separating solid and solution species during solubility measurements might affect the solution concentration by retention of soluble species, experiments were conducted to determine the degree of retention of U (VI) and Am (III) from very dilute solutions of nearly neutral pH by several different filter types typically used in solubility and sorption measurements. The different types of filters tested, along with the material, pore size and manufacturer, are given in Table 2.2. The alphabetical designation given to each type is used to identify them in subsequent tables.

Table 2.1. Fraction of Initial U(VI) in separated samples. Initial U(VI) concentration = 10^{-6} M, pH = 8.0±0.1.

Sample[a] equilibration time	Centrifugation (15,000 rmp-10 min.)	Filtration 0.20 μm	Filtration 0.015 μm
4 hours	0.864	0.790	0.461
	0.892	0.844	0.261
	0.878±0.020	0.844±0.076	0.361±0.141
2 hours	0.922	0.889	0.602
	0.952	0.946	0.549
	0.937±0.021	0.918±0.040	0.576±0.038
7 days	0.876	0.830	0.334
	0.872	0.884	0.417
	0.874±0.003	0.857±0.038	0.376±0.059

[a]Samples were run in duplicate

Table 2.2. Filters tested for retention of U (VI) and Am (III)

Filter	Pore Size (μm)	Material	Type-manufacturer
A	0.2	polysulfone	Acrodisc - Gelman Ann Arbor, Michigan
B	0.2	cellulose acetate	FP 03013 - Schleicher & Schüll Dassel, W. Germany
C	0.2	teflon	FP 030/8 - Schleicher & Schüll Dassel, W. Germany
D	0.45	cellulose acetate	C - Micro Filtration Systems Dublin, California
E	0.2	cellulose nitrate	A - Micro Filtration Systems Dublin, California
F	0.45	regenerated cellulose	G - Micro Filtration Systems Dublin, California
G	0.45	mixed cellulose acetate and nitrate	HA - Millipore Corp. Bedford, Mass.
H	0.2	polycarbonate	Standard Disk Membrane - Nuclepore Corp. Pleasanton, CA

First, 100-ml solutions of ^{233}U (VI) and ^{243}Am (III) were prepared in Nalgene bottles with 0.01 M NaCl as supporting electrolyte in an inert atmosphere box. The water used for preparation of solutions was again treated to remove CO_2. The starting solution concentrations were $9.868 \pm .103 \times 10^{-7}$ M for U and $2.833 \pm .071 \times 10^{-8}$ M for Am. Both the U and Am were first purified by cation-exchange chromatography (10). One bottle of each radionuclide had the pH adjusted to 5 and another to 8. The solutions were stirred and allowed to stand 2 days. After this time, the pH of the solutions were measured and 1-ml aliquots taken, mixed with scintillation "cocktail" solution, and their concentrations determined by alpha counting in the Packard liquid scintillation counter. The solution concentrations were less than the starting concentrations at this point due to loss of material to the walls of the bottles. Then, 3-ml portions of the solutions were passed through the different filters. The first ml through a filter was discarded. The concentration of uranium or americium in the subsequent 2 mls that passed through a filter was again determined by alpha counting. This procedure was carried out in duplicate for each filter. The results obtained in these measurements are given in Table 2.3 for uranium and Table 2.4 for americium. The tables contain the solution concentrations of uranium and americium after filtration and the percentage of the radionuclide present in the solution just before filtration that was retained by the filters.

From available thermochemical data, the hydroxides of U (VI) (13) and Am (III) (14) were not expected to precipitate at the starting solution concentrations and pH values used in the measurements. From data on the hydrolysis of U (VI) and Am (III), the U was calculated to be present in solution as 80% UO_2^{2+} and 20% $UO_2(OH)^+$ at pH 5, while Am was calculated

Table 2.3. Retention of U (VI) by filters

Filter	pH = 5.3 final conc. (M)	pH = 5.3 % retained	pH = 7.8 final conc. (M)	pH = 7.8 % retained
A	$8.680 \pm .322 \times 10^{-7}$	8.1	$5.198 \pm .193.10^{-7}$	19.5
	$9.268 \pm .344 \times 10^{-7}$	1.8	$5.188 \pm .192 \times 10^{-7}$	19.7
B	$7.401 \pm .274 \times 10^{-7}$	21.6	$5.014 \pm .186 \times 10^{-7}$	22.4
	$9.211 \pm .341 \times 10^{-7}$	2.4	$4.976 \pm .185 \times 10^{-7}$	22.9
C	$8.394 \pm .311 \times 10^{-7}$	11.1	$5.138 \pm .191 \times 10^{-7}$	20.4
	$8.639 \pm .320 \times 10^{-7}$	8.5	$5.048 \pm .187 \times 10^{-7}$	21.8
D	$9.026 \pm 335 \times 10^{-7}$	4.9	$3.741 \pm .139 \times 10^{-7}$	42.1
	$3.741 \pm .139 \times 10^{-7}$	60.3	$3.720 \pm .138 \times 10^{-7}$	42.4
E	$7.324 \pm .272 \times 10^{-7}$	22.4	$2.602 \pm .097 \times 10^{-7}$	59.7
	$8.772 \pm .325 \times 10-7$	7.1	$2.655 \pm .099 \times 10^{-7}$	58.9
F	$6.883 \pm .255 \times 10^{-7}$	27.1	$2.839 \pm .105 \times 10^{-7}$	56.0
	$6.584 \pm .244 \times 10^{-7}$	30.3	$3.413 \pm .122 \times 10^{-7}$	47.1
G	$8.487 \pm .325 \times 10^{-7}$	10.1	$3.943 \pm .146 \times 10^{-7}$	38.9
	$8.387 \pm .311 \times 10^{-7}$	11.2	$4.515 \pm .167 \times 10^{-7}$	30.1
H	$8.558 \pm .317 \times 10^{-7}$	9.3	$4.153 \pm .154 \times 10^{-7}$	35.7
	$8.412 \pm .312 \times 10^{-7}$	10.9	$4.548 \pm .169 \times 10^{-7}$	29.6

Starting concentration = $9.868 \pm .103 \times 10^{-7}$ M.

Concentration before filtration (pH=5.3)=$9.440 \pm .350 \times 10^{-7}$ M; retained by bottle = 4.3%.

Concentration before filtration (pH=7.8)=$6.457 \pm .239 \times 10^{-7}$ M; retained by bottle = 34.6%.

Table 2.4. Retention of Am (III) by filters

Filter	pH = 5.2 final conc. (M)	pH = 5.2 % retained	pH = 8.4 final conc. (M)	pH = 8.4 % retained
A	$1.492 \pm .065 \times 10^{-8}$	40.9	$1.186 \pm .052 \times 10^{-8}$	34.0
	$1.532 \pm .067 \times 10^{-8}$	39.4	$1.182 \pm .052 \times 10^{-8}$	34.2
B	$9.176 \pm .400 \times 10^{-9}$	63.7	$1.187 \pm .052 \times 10^{-8}$	33.9
	$8.575 \pm .374 \times 10^{-9}$	66.1	$1.195 \pm .052 \times 10^{-8}$	33.5
C	$1.840 \pm .080 \times 10^{-8}$	27.2	$8.439 \pm .368 \times 10^{-9}$	53.0
	$1.722 \pm .075 \times 10^{-8}$	31.9	$8.358 \pm .365 \times 10^{-9}$	53.5
D	$6.003 \pm .263 \times 10^{-9}$	76.2	$1.042 \pm .045 \times 10^{-8}$	42.0
	$6.610 \pm .289 \times 10^{-9}$	73.8	$1.012 \pm .044 \times 10^{-8}$	43.6
E	$5.617 \pm .246 \times 10^{-9}$	77.8	$8.838 \pm .386 \times 10^{-9}$	50.8
	$6.271 \pm .274 \times 10^{-9}$	75.2	$8.844 \pm .386 \times 10^{-9}$	50.7
F	$5.534 \pm .242 \times 10^{-9}$	78.0	$1.071 \pm .047 \times 10^{-8}$	40.4
	$5.365 \pm .235 \times 10^{-9}$	78.8	$1.076 \pm .047 \times 10^{-8}$	40.1
G	$5.178 \pm .227 \times 10^{-9}$	79.5	$9.545 \pm .416 \times 10^{-9}$	46.9
	$5.193 \pm .227 \times 10^{-9}$	79.4	$9.558 \pm .417 \times 10^{-9}$	46.8
H	$8.354 \pm .365 \times 10^{-9}$	66.9	$1.139 \pm .050 \times 10^{-8}$	36.6
	$9.378 \pm 409 \times 10^{-9}$	62.9	$1.108 \pm .048 \times 10^{-8}$	38.3

Starting concentration = $2.833 \pm .071 \times 10^{-8}$ M.

Concentration before filtration (pH=5.2)=$2.527 \pm .110 \times 10^{-8}$ M; retained by bottle = 10.8%.

Concentration before filtration (pH=8.4)=$1.796 \pm .078 \times 10^{-8}$ M; retained by bottle = 36.6%

to be present as greater than 99% Am^{3+}. At pH 8, the U was calculated to be present as 50% $UO_2(OH)_2^{\circ}$ and 50% $(UO_2)_3(OH)_7^{-}$ while Am was calculated to be present as 70% Am^{3+} and 30% $Am(OH)^{2+}$. Although other hydrolyzed species were also calculated to be present, they represented only very minor solution components.

As can be seen in Table 2.3, the amount of U retained by the bottles and filters is not great for pH values near 5 but is substantial for pH values near 8. As seen in Table 2.4, not much Am is retained by the bottle at a pH value near 5 but rather large amounts are lost at a pH value near 8. Substantial amounts of Am are retained by the filters at both pH values. Clearly, both U and Am are retained by the filters in varying degrees depending on the pH and nature of the filter.

Another series of measurements using Am were conducted to determine if the filters retain more of the radionuclide from the solution which passes through at the beginning of the filtration compared to later in the filtration, i.e., is there a saturation effect. Three-ml portions of a freshly prepared Am solution of pH = 8 were passed through the filters. The first 1.5 mls through the filters were collected separately from the second 1.5 mls and both were analyzed for the Am concentration. The results of these measurements are given in Table 2.5. Although there appeared to be small differences between the two fractions, there was no clear evidence of a saturation effect.

It was not clear at this point in the series of measurements whether the Am was being sorbed on filterable material (contaminants) in the solution or being sorbed on the filters themselves. Therefore, further measurements were made using an Am solution in which 3-ml portions were passed through the various filters. One ml of the filtrates was analyzed

Table 2.5. Retention of Am(III) by filters: filtrate split into two portions

Filter	First 1.5 mls		Second 1.5 mls	
	final conc. (M)	% retained	final conc. (M)	% retained
A	$1.673 + .073 \times 10^{-8}$	39.3	$1.765 \pm .077 \times 10^{-8}$	35.9
B	$1.949 \pm .085 \times 10^{-8}$	29.2	$1.991 \pm .087 \times 10^{-8}$	27.7
C	$1.507 \pm .066 \times 10^{-8}$	45.3	$1.410 \pm .061 \times 10^{-8}$	48.8
D	$1.865 \pm .081 \times 10^{-8}$	32.3	$1.878 \pm .082 \times 10^{-8}$	31.8
E	$1.504 \pm .065 \times 10^{-8}$	45.4	$1.576 \pm .069 \times 10^{-8}$	42.8
F	$1.727 \pm .075 \times 10^{-8}$	37.3	$1.835 \pm .080 \times 10^{-8}$	33.4
G	$1.332 \pm .058 \times 10^{-8}$	51.6	$1.407 \pm .061 \times 10^{-8}$	48.9
H	$1.964 \pm .086 \times 10^{-8}$	28.7	$1.856 \pm .081 \times 10^{-8}$	32.6

Starting concentration = $2.833 \pm .071 \times 10^{-8}$ M.

Concentration before filtration = $2.754 \pm .120 \times 10^{-8}$ M; retained by bottle = 2.8%.

pH = 5.0

for Am content while the remaining 2 mls were passed through a second filter of the same type before again being analyzed for Am content. The Am solution used for these determinations was the same as that used for the measurements reported in Table 2.4 under pH=8.4. The solution was by then about four weeks old; the pH had shifted to 6.6 and the percentage of Am sorbed by the bottle had increased. The results are presented in Table 2.6. The general trend was that the second filter removed only about one half as much Am from solution as did the first filter. These data suggest, but do not conclusively demonstrate, that the Am may have been sorbed on filterable material in the solution, e.g. silica or dust particles, as well as sorbed by the filters themselves.

Finally, measurements were made to determine if pretreatment of the filters with a dilute acid wash would change the retention characteristics of the filters, e.g. by removing foreign material. The various filters were washed by passing 3 mls of 0.5 M HCl through them followed by 3 mls of distilled water. The filters were then vacuum dried. Three-ml portions of a freshly prepared Am solution of pH = 5 were passed through both treated and untreated filters of the various types. The filtrates were analyzed for Am content.

The results are given in Table 2.7. The data indicate that, while a reduction in the retention of Am occurred for two of the filter types after pretreatment, most of the filters were unaffected by the acid wash and the amount of Am retained by one of the filters substantially increased.

2.2.3 Comparison of Separation Methods

Experiments were conducted to test and compare three commonly used methods for the separation of solid and aqueous phases in solubility measurements,

Table 2.6. Retention of Am (III) by Two Successive Filters

Filter		Final conc.(M)	% Retained
A	(1)	$9.515 \pm .415 \times 10^{-9}$	28.1
	(2)	$8.843 \pm .386 \times 10^{-9}$	7.1
B	(1)	$7.876 \pm .344 \times 10^{-9}$	40.5
	(2)	$6.505 \pm .284 \times 10^{-9}$	17.4
C	(1)	$1.121 \pm .049 \times 10^{-8}$	15.3
	(2)	$9.090 \pm .397 \times 10^{-9}$	18.9
D	(1)	$6.231 \pm .272 \times 10^{-9}$	52.9
	(2)	$4.999 \pm .219 \times 10^{-9}$	19.8
E	(1)	$6.322 \pm .276 \times 10^{-9}$	52.2
	(2)	$5.061 \pm .222 \times 10^{-9}$	19.9
F	(1)	$5.597 \pm .245 \times 10^{-9}$	57.7
	(2)	$4.514 \pm .198 \times 10^{-9}$	18.7
G	(1)	$7.068 \pm .309 \times 10^{-9}$	46.6
	(2)	$4.742 \pm .208 \times 10^{-9}$	32.9
H	(1)	$6.544 \pm .286 \times 10^{-9}$	50.5
	(2)	$4.696 \pm .206 \times 10^{-9}$	28.2

Starting concentration = $2.833 \pm .071 \times 10^{-8}$ M.

Concentration before filtration = $1.323 \pm .058 \times 10^{-8}$ M; retained by bottle = 53.3%.

pH = 6.6

(1) = first filtration; (2) = second filtration

Table 2.7. Retention of Am (III) by Acid Treated and Untreated Filters

Filter	Treated		Untreated	
	final conc. (M)	% retained	final conc. (M)	% retained
A	$1.885 \pm .082 \times 10^{-8}$	27.7	$1.499 \pm .063 \times 10^{-8}$	42.5
B	$1.295 \pm .056 \times 10^{-8}$	50.4	$1.067 \pm .047 \times 10^{-8}$	59.1
C	$1.203 \pm .053 \times 10^{-8}$	53.9	$1.516 \pm .066 \times 10^{-8}$	41.9
D	$1.118 \pm .049 \times 10^{-8}$	57.1	$1.241 \pm .054 \times 10^{-8}$	52.4
E	$1.001 \pm .044 \times 10^{-8}$	61.6	$1.611 \pm .070 \times 10^{-8}$	38.2
F	$2.559 \pm .111 \times 10^{-8}$	1.9*	$1.015 \pm .044 \times 10^{-8}$	61.1
G	$9.203 \pm .401 \times 10^{-9}$	64.7	$9.433 \pm .411 \times 10^{-9}$	63.8
H	$1.955 \pm .085 \times 10^{-8}$	25.0	$1.171 \pm .051 \times 10^{-8}$	55.1

*Filter failed

Starting concentration = $2.833 \pm .071 \times 10^{-8}$ M.

Concentration before filtration = $2.608 \pm .113 \times 10^{-8}$ M; retained by bottle = 8.0%

pH = 5.0

i.e. gravity settling, filtration and centrifugation. For these measurements, solutions containing ^{238}U (VI) and ^{243}Am (III) were prepared in 0.01 M NaCl at pH values of about 5 and 9, and in a simulated basalt ground water. In some of the cases, precipitation of the hydroxides of U (VI) and Am (III) were expected to occur. After separation of aqueous and solid phases using each of the three separation methods, final solution concentrations were determined and compared.

The ^{238}U, "spiked" with ^{233}U for counting purposes, and the ^{243}Am were purified and oxidation state selection made by cation-exchange chromatography. First, samples containing 10 mls of $1.00 \pm .03 \times 10^{-4}$ M U (VI) and $1.13 \pm .03 \times 10^{-7}$ M Am (III) were prepared in glass bottles with 0.01 M NaCl as supporting electrolyte. Two bottles of each radionuclide had their pH adjusted to 5.0 and 9.0, i.e. duplicate samples. Two samples of each radionuclide were also prepared with a simulated basalt groundwater as supporting electrolyte. A reference basalt groundwater (15) was used and the composition is given in Table 2.8. Pretreated, distilled water and ultrapure HCl, NaOH and NaCl were used in the preparation of the solutions with NaCl as supporting electrolyte. Before use, the water was passed through 0.2 μm diameter pore size Nuclepore filters to remove filterable contaminants. The same water and analytical grade $NaHCO_3$, KCl, $CaCl_2$, $MgCl_2$, NaF, Na_2SO_4, NaCl and H_4SiO_4 obtained from Mallinckrodt Inc. were used for the preparation of the simulated groundwater. Preparation of the solutions and subsequent manipulations of the samples were done in an inert atmosphere box under argon. The solutions were allowed to equilibrate for 84 days. During this time, the solutions were stirred and their pH values measured periodically. If necessary, the pH of each was adjusted back to

Table 2.8. Composition of Simulated Basalt Groundwater

component	concentration (mg/l)
Na^+	250
K^+	1.9
Ca^{2+}	1.3
Mg^{2+}	0.04
HCO_3^-	46
SO_4^{2-}	108
Cl^-	148
F^-	37
H_4SiO_4	147
pH	9.7

the original value. After this period, the solutions were allowed to stand undisturbed for a week to permit separation of solid and aqueous phases by gravity settling. The final pH values of the solutions were determined and one ml aliquots taken. Each aliquot was mixed with 14 mls of scintillation cocktail and the concentrations of U and Am determined by gross alpha counting of the mixtures in the Packard scintillation counter. Then, 1.25-ml aliquots of the solutions were taken and centrifuged at 15,000 rpm for 10 minutes. One ml of each supernatant was taken and the U and Am concentrations determined as before by scintillation counting. Finally, 3-ml aliquots of the solutions were taken and passed through 0.2 μM pore size Gelman acrodisc filters. One ml of each filtrate was taken and again the U and Am concentrations determined by alpha scintillation counting.

The final U and Am concentrations (moles/liter) measured in the three differently separated aqueous phases are given in Tables 2.9 and 2.10, respectively. The stated probable errors in the concentrations result only from a consideration of counting statistics and the reproducibility of sampling volumes.

From calculations using available data on the solubilities of freshly precipitated hydroxides of U (VI) (13) and Am (III) (14), the following approximate final solution concentrations were expected:

U - 2.5×10^{-5} M at pH=5.5, 3×10^{-5} M at pH=9.0, 4×10^{-5} M at pH=9.7.

Am - no precipitation at pH=5.0, 2.5×10^{-8} M at pH=8.8, 2.5×10^{-9} M at pH-9.7.

The final concentrations given in Tables 2.9 and 2.10 are in reasonable agreement with these expected values except for the simulated groundwater.

Table 2.9. Final Uranium Solution Concentrations as Determined by Three Separation Methods

Sample	pH[a]	Final U Conc. (M)		
		Gravity Settling	Filteration	Centrifugation
1[b]	5.49	$6.47 \pm .34 \times 10^{-5}$	$5.92 \pm .31 \times 10^{-5}$	$5.90 \pm .31 \times 10^{-5}$
2	5.74	$6.40 \pm .33 \times 10^{-5}$	$5.39 \pm .28 \times 10^{-5}$	$5.33 \pm .28 \times 10^{-5}$
1[b]	9.09	$7.20 \pm .38 \times 10^{-5}$	$7.02 \pm .37 \times 10^{-5}$	$7.31 \pm .38 \times 10^{-5}$
2	9.10	$7.60 \pm .40 \times 10^{-5}$	$7.45 \pm .39 \times 10^{-5}$	$7.56 \pm .39 \times 10^{-5}$
1[c]	9.77	$9.97 \pm .52 \times 10^{-5}$	$9.95 \pm .52 \times 10^{-5}$	$9.90 \pm .52 \times 10^{-5}$
2	9.75	$9.99 \pm .52 \times 10^{-5}$	$9.86 \pm .51 \times 10^{-5}$	$1.01 \pm .53 \times 10^{-4}$

Starting U conc. = $1.00 \pm .03 \times 10^{-4}$ M

a. Error in pH = ± 0.1
b. 0.01 M NaCl supporting electrolyte
c. Simulated basalt groundwater

Table 2.10. Final Americium Solution Concentrations as Determined by Three Separation Methods

Sample	pH[a]	Final Am Conc. (M)		
		Gravity Settling	Filteration	Centrifugation
1[b]	4.94	$9.92 \pm .49 \times 10^{-8}$	$9.19 \pm .45 \times 10^{-8}$	$1.01 \pm .05 \times 10^{-7}$
2	4.99	$1.00 \pm .05 \times 10^{-7}$	$9.46 \pm .47 \times 10^{-8}$	$9.97 \pm .49 \times 10^{-8}$
1[b]	8.77	$4.77 \pm .24 \times 10^{-8}$	$3.77 \pm .19 \times 10^{-8}$	$3.70 \pm .18 \times 10^{-8}$
2	8.91	$4.57 \pm .23 \times 10^{-8}$	$4.00 \pm .20 \times 10^{-8}$	$3.46 \pm .17 \times 10^{-8}$
1[c]	9.67	$6.15 \pm .31 \times 10^{-8}$	$5.94 \pm .29 \times 10^{-8}$	$6.08 \pm .30 \times 10^{-8}$
2	9.76	$6.77 \pm .34 \times 10^{-8}$	$6.58 \pm .33 \times 10^{-8}$	$6.80 \pm .34 \times 10^{-8}$

Starting Am conc. = $1.13 \pm .03 \times 10^{-7}$ M

a. Error in pH = ± 0.1
b. 0.01 M NaCl supporting electrolyte
c. Simulated basalt groundwater

The groundwater values are considerably higher than expected for a pH of 9.7. This increase in solubility of both U and Am might be due to the formation of carbonate complexes in solution.

Filtration of the water before preparation of solutions appears to have substantially reduced losses due to psuedocolloid formation. For the measurements described in Section 2.2.2, the water was not filtered and a minimum of 30% and as much as 80% of the Am was retained by the various filters for a solution pH near 5 (see Tables 2.4 and 2.6 for example). In these experiments where the water was filtered, only 10-15% of the Am was lost from solution under similar solution conditions and part of this loss is probably due to the sorption by container walls.

In general, where precipitation had occurred, separation of solid and aqueous phases by gravity settling tended to result in slightly higher final solution concentrations than separation by filtration and centrifugation. Separation by filtration and centrifugation gave results that agreed within experimental error.

3.0 CONCLUSION AND RECOMMENDATIONS

The experimental results indicate that when dealing with trace amounts of radionuclides in solution, e.g. concentrations of 10^{-6} M or less, losses of the radionuclide from solution by sorption on container walls and by retention by filters during the filtration process can occur even under conditions when a solubility product is not exceeded. These losses could potentially affect the accurate measurement of solution concentrations in solubility determinations. The amount of the radionuclides retained by the filter depends on the pH of the solution and on the nature of the filter. This retention may be due in part to sorption of soluble species onto filterable material present in the water, i.e. contaminants that produce psuedocolloids, but some retention also appears to result from sorption of soluble species by the filters themselves. The former can be substantially reduced by filtration of the water or reagent solutions before use in the actual experiment.

Sorption by container walls would probably not be a problem in actual solubility measurements if there is excess solid phase and the solid, walls and solution phases are allowed to come to equilibrium. Otherwise, the amount of radionuclide sorbed by the walls should be determined and a correction made if necessary.

Of the three separation methods tested, centrifugation appears to be the most likely to yield accurate results in general. However, it should be determined if the centrifuge can exert sufficient force to precipitate the appropriate particle sizes. Separation by gravity settling tended to yield higher solution concentrations than the other two methods. Whether this was due to a deficiency in the separation process itself or

to resuspension of the loosely packed and finely divided solid material during sampling or other handling was not determined. In our experiments to compare the three separation methods, filtration gave solution concentrations which were the same as centrifugation to within experimental error. However, we had selected a filter that showed only a small amount of sorption of soluble species in our earlier experiments. If filters are used for separations, care must be taken to select a type that has been demonstrated to not appreciably alter the solution concentration by the filtration process itself, e.g. by a double or triple filtration technique.

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