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THE INFLUENCE OF DISSOLVED ORGANIC SUBSTANCES IN GROUNDWATER
ON SORPTION BEHAVIOR OF AMERICIUM AND NEPTUNIUM

by

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Chemical Technology Division

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S. Boggs, Jr.,[†] and M. G. Seitz

ABSTRACT

Groundwaters typically contain dissolved organic carbon consisting largely of high molecular weight compounds of humic and fulvic acids. To evaluate whether these dissolved organic substances can enhance the transport of radionuclides through the groundwater system, experiments were conducted to examine the sorption of americium and neptunium onto crushed basalt in the presence of dissolved humic- and fulvic-acid organic carbon introduced into synthetic groundwater.

The partitioning experiments with synthetic groundwater show that increasing the concentration of either humic or fulvic acid in the water has a significant inhibiting effect on sorption of both americium and neptunium. At 22°C, adsorption of these radionuclides, as measured by distribution ratios (the ratio of nuclide sorbed onto the solid to nuclide in solution at the end of the experiment), decreased by 25% to 50% by addition of as little as 1 mg/L dissolved organic carbon and by one to two orders of magnitude by addition of 100-200 mg/L dissolved organic carbon. Distribution ratios measured in solutions reacted at 90°C similarly decreased with the addition of dissolved organic carbon but generally ranged from one to two orders of magnitude higher than those determined in the 22°C experiment. These results suggest that organic carbon dissolved in deep groundwaters may significantly enhance the mobility of radionuclides of americium and neptunium.

I. INTRODUCTION

The migration of radionuclides in the groundwaters of shallow radioactive waste disposal sites has been shown to be enhanced by the presence of synthetic organic compounds, such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), cyclohexanediaminetetraacetic acid (CDTA), and diethylenetriamine pentaacetic acid (DTPA), that are widely used in nuclear cleanup operations [CLEVELAND, MEANS-1978, WEISS]. The complexing behavior of these synthetic organic compounds with radionuclides suggests the possibility that natural organic compounds in groundwaters, which can also have high complexing ability [SCHNITZER], may likewise influence the migration of radionuclides. The potential effects of natural organic substances in the groundwater system on actinide elements that may escape from high-level

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radioactive waste repositories are of particular concern. Available data show that the concentration of total dissolved organic carbon (DOC) in groundwaters from deep wells in granitic and basaltic rocks at potential waste repository sites ranges from less than 1 mg/L to as much as 20 mg/L [MEANS-1982]. Concentrations of DOC reach much higher values (12 to 76 mg/L) in deep wells of oil-producing basins such as the Paradox and Permian Basins [MEANS-1983]. Such high values are exceptional, and most deep groundwaters probably contain less than 2 to 3 mg/L total DOC. In fact, [LEENHEER] found that the mean concentration of DOC in 100 groundwaters from sandstones, limestones, and crystalline rocks at depths of 10 to 400 m was 1.2 mg/L.

Many kinds of dissolved organic substances occur in groundwater, including amino acids, fatty acids, phenols, sterols, natural sugars, hydrocarbons, urea, and porphyrins; however, much of the organic carbon in groundwater is derived from humic substances and consists of humic and fulvic acids [MEANS-1981]. Humic substances are complex mixtures of organic species of high molecular weight and poorly known structure that are generally classified on the basis of solubility. Humic acid is that fraction of humic substances that is soluble in a base; fulvic acid is that fraction that is soluble in both acid and base; and humin is the insoluble fraction that cannot be extracted by either acid or base. About 85% of the dissolved humic substances in natural groundwaters consists of fulvic acid and 15% consists of humic acid [THURMAN].

The ability of natural organic substances in surface waters and soils to form complexes with radionuclides has been studied by several investigators; reports include [BONDIETTI, CLAYTON, CLEVELAND, NELSON]. In additional studies, [NASH] studied the sorption of U, Pu, and Np by clay particles in a seawater environment. Equivalent studies to investigate the complexing of natural organic carbon in deep groundwaters are still in the initial stages (e.g., MEANS-1983), and experimental data are very few.

As an initial step to addressing this deficiency, we conducted the experiments described here to examine the effects of organic carbon in groundwaters on the sorption of americium and neptunium. Progress in this program has been presented in three quarterly reports [STEINDLER-1983A, -1983B, -1983C]. Initial work focused on batch partitioning experiments with crushed basalt and synthetic groundwater to which measured concentrations of either humic acid or fulvic acid were added. This report discusses the techniques used in these batch partitioning experiments and describes the experimental results.

II. METHODS

A. Sample Preparation

1. Synthetic Groundwater

Synthetic groundwater having about the same chemical composition as the groundwater at the Hanford, Washington, site [GEPHART] was prepared by adding the compounds shown in Table 1 to 20 L of deionized water. The solution was mixed on a magnetic stirring plate and sparged with N₂ gas to eliminate CO₂, which could affect the pH. The solution was then filtered

Table 1. Preparation and Composition of Synthetic Groundwater

Compound	Major Constituent	Quantity Added to 20 L of Deionized Water, ^a g	Quantity in Solution, mg/L	
			Calculated ^a	Measured ^b
NaCl		3.115		
Na ₂ SO ₄		3.194		
Na ₂ B ₄ O ₇ ·10H ₂ O		0.245		
NaF		1.636		
NaCO ₃		1.201		
NaHCO ₃		1.184		
Na ₂ SiO ₃ ·9H ₂ O		11.463		
K ₂ SO ₄		0.085		
CaSO ₄ ·2H ₂ O		0.111		
MgSO ₄ ·7H ₂ O		0.0036		
HCl (1N)		24 mL		
	Na		302	300
	Cl ⁻		148	226
	SO ₄ ⁻²		114	107
	B		1.39	1.30
	F ⁻		37	32
	CO ₃ ⁻²		34	25.8 ^c
	HCO ₃ ⁻		43	50.0 ^c
	Si		56	41
	K		1.9	1.9 ^c
	Mg		0.04	<0.01
	Ca		1.3	1.02
pH:			10.1	9.92

^aBatch No. 4.^bBatch No. 1, except as noted.^cBatch No. 3.

through a 0.2- μ m pore size filter (of mixed esters of cellulose acetate and nitrate) to remove particulates. The pH of the water after sparging with nitrogen was 10.1, equal to the pH of groundwater at the Hanford site. Several batches were prepared.

2. Humic and Fulvic Acid

Commercial humic acid (Fluka-AG, Buchs-SG), obtained from Triodom Chemical Company, was purified prior to its use in the experiment by removing complexing metals and ash by the following procedure. Ten grams of dry humic acid were treated with 75 mL of 2M HCl for two hours to remove iron oxides. The sample was then washed repeatedly with deionized water until a negative test for chloride ion was obtained. Following the procedure of [NASH], the humic acid was dissolved in about 400 mL of 0.1M NaOH, placed in a polyethylene bottle with about 100 g of DOWEX AG-50W-10X (20-50 mesh) ion-exchange

resin in the Na^+ form, and rotated on a mixer for 30 hours to remove metal ions. The dissolved humic acid was decanted and washed from the resin with deionized water, and acidified with 2M HCl to a pH of about 2 to precipitate the humic acid, which was separated by centrifugation. The solid humic acid was then washed thoroughly in distilled water until all chloride ions were removed, and dried in a rotating evaporator at 70°C . Total yield of dry humic acid was 4.64 g.

Dried fulvic acid extracted from soils collected in the San Juan Islands was provided for the experiments by Dr. C. Langford, Concordia University, Montreal, Canada. The fulvic acid was previously purified and treated in an ion-exchange column in Dr. Langford's laboratory.

Stock solutions of humic and fulvic acid were prepared by mixing 0.5 g each of the dried, purified acids in separate containers with 100 mL of synthetic groundwater. Both acids dissolved readily in the high-pH groundwater. The solutions were stirred for 72 hours and filtered through a $0.4\text{-}\mu\text{m}$ Nuclepore filter. The total dissolved organic carbon (DOC) of each stock sample was determined by analysis on a Sybron/Barnstead Photochem Organic Carbon Analyzer. Aliquots of the stock humic-acid solution, measured to contain 330 mg/L of DOC, were added to synthetic groundwater solutions containing either americium or neptunium to yield test solutions of either humic acid plus americium or humic acid plus neptunium with DOC concentrations of 1, 10, 20, 100, and 200 mg/L (Table 2). A test solution containing no humic-acid DOC was also prepared. A similar batch of test solutions having the same concentrations of DOC was prepared from the fulvic-acid stock solution, which was measured to contain 400 mg/L of DOC.

The addition of organic acids and reaction of the solutions with basalt modified the pH of the synthetic groundwaters. These changes were monitored because pH is an important parameter in the sorption of nuclides. In addition, some solutions were titrated to a fixed pH value prior to experimentation so that the effects of organic acids could be distinguished from the effects of pH.

As evident from analyses of the stock solutions, the purified humic and fulvic acids contained measurable quantities of the inseparable metals, Fe, Al, Ca, Cr, Ti, Zn, Mg, Zr, and Cu. These quantities ranged from 0.36% and 0.092% (both Fe) to 0.0025% (Zr) and 0.0015% (Cu) in the dried humic and fulvic acids, respectively.

3. Radionuclides

The nuclide ^{241}Am in a 0.1N solution of HCl was added to about 400 mL of synthetic groundwater to produce the americium spike used in the test solutions. This isotope of americium decays with a 432-year half-life by emitting an alpha particle with concomitant release of a 59.5-keV gamma ray. The decay can be detected by both alpha and gamma counting. The initial concentrations of americium in the test solutions ranged from 1 to $9 \times 10^{-10}\text{M}$, as determined from the specific activities of the solutions--250 to $1700\text{ d}/(\text{min}\cdot\text{mL})$.

The nuclide ^{237}Np was dried from a solution of 1N HCl , then dissolved in 400 mL of groundwater to form the spike solution. This isotope of neptunium has a half-life of 2.14×10^6 years, decaying by emission of an

Table 2. Test Solutions of Humic and Fulvic Acid in Synthetic Groundwater Used in Batch Partitioning Experiments with Americium and Neptunium

Test-Solution Number	Type of Solution	Total DOC, mg/L	pH at 22°C
1-HA	Synthetic Groundwater	0	9.92
2-HA	Humic Acid ^a	1	9.94
3-HA	Humic Acid	10	9.86
4-HA	Humic Acid	20	9.84
5-HA	Humic Acid	100	9.50
6-HA	Humic Acid	200	8.79
1-FA	Synthetic Groundwater	0	9.92
2-FA	Fulvic Acid ^b	1	10.09 ^c
3-FA	Fulvic Acid	10	10.04 ^c
4-FA	Fulvic Acid	20	10.00 ^c
5-FA	Fulvic Acid	100	9.58 ^c
6-FA	Fulvic Acid	200	8.52 ^c

^aThe humic-acid solutions were prepared by mixing the stock humic-acid solution containing 330 mg/L DOC with synthetic groundwater batch No. 4. The dried humic acid contained 0.359% Fe, 0.087% Ti, 0.053% Al, 0.031% Ca, 0.020% Cu, 0.0061% Zn, 0.0047% Mg, and 0.0025% Zr, presumed to be complexed metals.

^bThe fulvic-acid solutions were prepared by mixing the stock fulvic-acid solution containing 400 mg/L DOC with synthetic groundwater batch No. 4. The dried fulvic acid contained 0.092% Fe, 0.045% Al, 0.043% Ca, 0.0056% Zn, 0.0038% Mg, 0.0036% Cr, 0.0025% Zr, 0.0023% Ti, and 0.0015% Cu, presumed to be complexed metals.

^cpH measurements were of fulvic acid in synthetic groundwater batch No. 5, which initially had a pH of 10.1.

alpha particle of 4.77 MeV and a gamma ray of 86.5 keV. The decay of ²³⁷Np detectable by both alpha and gamma counting. The initial concentrations neptunium in the test solutions ranged from 0.7 to 3 x 10⁻⁶M, as determined from the solution specific activities--250 to 1150 d/(min·mL).

4. Crushed Basalt

The rock used in this study as a sorption medium for americium and neptunium is unweathered basalt from the Pomona Member (aged about 14 million years) of the Columbia River Group from the Pasco Basin of Washington. Chemical analyses of rock samples and mineral separates from this flow are given by [AMES]. The basalt was crushed and sieved through No. 60 and No. 80 mesh sieves to yield a size fraction ranging from 0.18 to 0.25 mm. The sieved fraction was washed in deionized water to remove fine dust clinging to the grains and was dried for 18 hours in an oven at 60°C.

B. Experimental Procedures

Samples were prepared for batch testing by first placing about 0.5 g of granulated Pomona basalt in each of 36 glass vials having screw tops with Teflon seals and 10-mL capacity. A 5-mL aliquot of each test solution shown in Table 2 was added to each of six vials, yielding six replicate batch samples at each DOC concentration--a total of 36 samples. One group of 18 vials (three replicates of each test sample) was placed on a rotator that turned the vials end-for-end at a low speed; the vial contents were allowed to react for seven days at ambient temperature (22°C). The remaining group of 18 vials (likewise three replicates) was placed on another rotator in an oven set at 90°C, with the reaction continuing for seven days, also.

After the seven days, the sample vials were removed and centrifuged for 15 minutes. A 1-mL aliquot of each sample solution was withdrawn for gamma counting. The remaining liquid was then withdrawn from the vials with a syringe and filtered through a 0.45- μ m Metrical membrane filter. A 1-mL aliquot of this filtered liquid was separated for gamma counting, and the additional liquid was retained for alpha detection by scintillation counting. The granulated basalt remaining in the vials was rinsed quickly with deionized water and was transferred to test tubes for gamma counting. The glass vials were retained to check for gamma activity.

Gamma activity in each liquid sample was determined by counting for 1000 seconds on a 3-inch sodium iodide well detector. Alpha activity was measured by mixing 1 mL of a test solution with 20 mL of Insta-Gel* scintillation liquid and counting for 60 minutes. To avoid quenching of the scintillations due to the organic content of test solutions having 100 and 200 mg/L DOC, only 0.25-mL aliquots of these solutions were used, together with 0.75 mL of synthetic groundwater and 20 mL of Insta-Gel for counting.

The activity in samples of the original test solutions (before reacting with basalt) was counted to allow final activity in the solutions to be compared with initial activity. Also, some unfiltered solutions were counted after centrifugation so that the effect of filtering could be noted. The filtering removed active suspended particulate in some cases and, so, filtering was performed prior to all analyses reported here.

The activity remaining in each of the test solutions after reacting with crushed basalt was subtracted from the initial activity in them to determine the amount lost from the solutions during the experiments by sorption onto

* Trade name of the Packard Instrument Company.

the basalt and onto the walls of the test vials. The activity sorbed onto the walls of the vials was subsequently measured to be less than 2% of the original activity in the samples. The small error caused by sorption onto the walls of the vials is considered negligible and is ignored in calculating distribution ratios. The measured radioactivities of the starting and final solutions, together with calculations of the distribution ratios, are reported elsewhere [STEINDLER-1983A, -1983B, -1983C]. The distribution ratio (R_d), expressed in mL/g, is the ratio of nuclide on the solid to nuclide in solution at the end of the experiment, and was calculated by the equation

$$R_d = \frac{\text{activity/gram of rock}}{\text{activity/milliliter of solution}}$$

where activity on the rock (basalt) is determined by subtracting the final activity in the solution from the initial activity. This procedure avoids the error due to attenuation of gamma activity that occurs by counting the activity of the basalt directly. The empirical ratio does not imply equilibrium conditions, quantitative reversibility, or ion exchange in the processes governing sorption. An increase in R_d value signals a decreased amount of radionuclide in the groundwater and, hence, a reduced ability to migrate with moving groundwater.

The R_d values derived in these experiments were assumed to be from normally distributed populations. Because the data used to determine all R_d values were measured in the same fashion, it is reasonable to assume that the R_d values at every concentration of humic or fulvic acid had the same variance. On this basis, the distribution of data was tested using the t-statistic compared to Student's t distribution. The confidence levels at which the R_d values at different concentrations of fulvic or humic acid can be considered to be different are given in subsequent sections of this report, together with tabulated arithmetic means and standard deviations from replicate determinations of the distribution ratios.

III. EFFECTS OF REACTION WITH BASALT ON SOLUTION pH AND CHEMISTRY

The pH and inorganic chemical compositions of groundwaters are known to affect nuclide sorption. Nuclide adsorption for alkali and alkaline earth elements, for example, show consistent decreases in distribution ratios as the groundwater Na^+ and Ca^{+2} concentrations increase [SERNE]. We were interested to learn if significant changes in solution chemistry would take place as a result of reaction with granulated basalt during the batch partitioning experiments, and if the concentration of humic-acid dissolved organic carbon (DOC) in the solution affected the magnitude of these changes. To investigate these issues, we analyzed pH and chemical changes of groundwater solutions containing various concentrations of humic acid that were reacted with basalt.

A. Procedure

To investigate the changes in pH and chemical composition that take place as a result of the reaction of the groundwater with basalt, we prepared nuclide-free solutions with concentrations of humic-acid DOC the same as those used in the batch partitioning experiments. The initial pH and

chemical composition of these solutions were measured. After solutions containing different concentrations of humic acid were reacted with granulated basalt for seven days at 22°C and 90°C, the solutions were filtered, the pH was measured, and a sample of each solution was analyzed for chemical composition. The pH was measured using a glass body combination electrode with a calomel reference junction. The instrument was calibrated in the pH range of 4.01 to 10.00 using buffers standardized against NBS certified pH references and accurate to ± 0.01 pH units.

B. Results

Values of pH with respect to different concentrations of humic acid before and after reaction of the solutions with granulated basalt at 22°C and 90°C are shown in Table 3. Before reaction, an increase in humic-acid DOC from 0 to 20 mg/L produced only a minor decrease in pH; however, an

Table 3. Changes in the pH of Solutions Used in Batch Experiments as a Result of Changes in the Concentration of Dissolved Humic Acid and Reaction with Granulated Pomona Basalt for Seven Days

Test-Solution Number	Humic-Acid DOC, mg/L	pH Measured at	
		90°C	22°C
<u>Before Reaction</u>			
1-HA	0		9.92
2-HA	1		9.94
3-HA	10		9.86
4-HA	20		9.84
5-HA	100		9.50
6-HA	200		8.79
<u>After Reaction at 22°C</u>			
1-HA	0		9.54
2-HA	1		9.55
3-HA	10		9.51
4-HA	20		9.50
5-HA	100		9.13
6-HA	200		8.60
<u>After Reaction at 90°C</u>			
1-HA	0	8.10	8.63
2-HA	1	8.16	8.81
3-HA	10	8.07	8.78
4-HA	20	8.07	8.72
5-HA	100	7.86	8.50
6-HA	200	7.56	8.22

increase in DOC to 200 mg/L decreased the pH by more than 1 pH unit--from 9.92 to 8.79. Reaction of the humic-acid solution with granulated basalt also produced a significant decrease in pH after seven days, particularly in the solutions reacted at 90°C, in which the pH decreased by amounts ranging from 0.6 to 1.3 pH units.

The composition of each solution before reacting with basalt is shown in Table 4. The mixing of the dried humic acid with the synthetic groundwater to prepare the humic-acid stock solution increased the concentration of several elements above the levels originally present in the groundwater. In particular, the concentrations of Fe, Si, Al, Cr, Cu, Ti, and Zr are higher, reflecting the presence of these elements in the dried humic acid.

The compositions of batch-experiment solutions after reaction with basalt is shown in Table 5. Anion concentration remained about the same in all solutions and apparently is little affected by the humic-acid concentration. On the other hand, many of the cations, particularly trace-metal ions, show an increase in concentration after reaction with basalt.

After reaction with basalt, the concentrations of Ca, Si, Mg, Mn, Al, Fe, Cr, Sr, and F⁻ increased in all test solutions in both the 22°C and 90°C experiments, and the concentration of B, Ni, and V increased in the 90°C experiment only. Increase in silica concentration was greatest in the 90°C test solutions, whereas the increase in iron was greatest in the 22°C test solutions. Concentrations of Cu, Zn, Zr, and Ti increased in some solutions but decreased in others. The observed increase in concentration of several cations and F⁻ is probably due primarily to selective dissolution of these ions from the surface of the crushed basalt. Cation exchange may also be responsible for some of the observed change, particularly the sharp decrease in Na concentration and corresponding increase in Ca and Mg. The significant loss of Cl⁻ from all solutions cannot, however, be accounted for by ion exchange and is more likely due to formation of clay minerals on the surface of the basalt. Formation of clay minerals could also cause a decrease in Na levels in the solutions. No attempt to identify the new mineral phases was made in this work.

The concentration of humic-acid DOC in the solutions clearly affected final solution chemistry. Concentrations of Ca, Mg, Fe, Mn, Ni, and Sr are consistently higher in solutions containing 20 mg/L or more DOC than in the solutions with 10 mg/L or less. The concentrations of these elements in solutions containing 100 and 200 mg/L DOC are an order of magnitude or more higher than in solutions containing 10 mg/L or less. The higher concentrations of these metals would be expected to lessen the measured dependence of the R_d value on DOC because the metals compete with radionuclides to complex with the organic molecules.

Table 4. Chemical Compositions of Batch-Experiment Solutions before Reaction

Test-Solution Number	Humic-Acid DOC, mg/L	Constituent, mg/L								
		Na	Ca	Mg	Si	B	Fe	Al	Cl ⁻	SO ₄ ⁻²
1-HA	0	300	1.02	<0.01	41	1.3	<0.02	<0.03	226	107
2-HA	1	300	1.02	<0.01	41	1.3	0.03	<0.03	226	107
3-HA	10	300	1.03	<0.01	41	1.3	0.13	0.05	226	107
4-HA	20	300	1.04	<0.01	41	1.3	0.23	0.06	226	107
5-HA	100	299	1.10	0.02	43	1.3	1.09	0.18	227	108
6-HA	200	298	1.19	0.03	44	1.4	2.17	0.33	228	109
Humic-Acid Stock Solution	330	297	1.3	0.05	46	1.4	3.6	0.53	229	110

Constituent, mg/L										
	F ⁻	Cr	Cu	Mn	Ni	Sr	Ti	V	Zn	Zr
1-HA	32	<0.02	<0.02	<0.005	<0.02	<0.005	<0.005	<0.02	<0.01	<0.01
2-HA	32	<0.02	<0.02	<0.005	<0.02	<0.005	<0.005	<0.02	<0.01	<0.01
3-HA	32	0.02	0.02	<0.005	<0.02	<0.005	<0.01	<0.02	<0.01	<0.01
4-HA	32	0.03	0.03	<0.005	<0.02	<0.005	0.01	<0.02	0.01	<0.01
5-HA	32	0.08	0.08	<0.005	<0.02	<0.005	0.03	0.02	0.03	0.01
6-HA	32	0.13	0.13	<0.005	<0.02	<0.005	0.05	<0.02	0.04	0.02
Humic-Acid Stock Solution	32	0.02	0.02	<0.005	<0.02	<0.005	0.87	<0.02	0.06	0.03

Table 5. Compositions of Batch-Experiment Solutions after Reacting with Granulated Pomona Basalt for Seven Days

Test-Solution Number ^a	Humic-Acid DOC, mg/L	Constituent, mg/L										
		Na	Ca	Mg	Si	B	Fe	Al	Cl ⁻	SO ₄ ⁻²	F ⁻	Alkalinity ^b
After Reaction at 22°C												
1-HA	0	289	6.5	2.1	46.1	1.4	0.78	0.22	191	100	37	c
2-HA	1	284	6.2	2.0	44.2	1.4	1.2	0.16	189	91	38	c
3-HA	10	279	6.6	2.0	41.9	1.3	1.8	0.15	186	91	38	c
4-HA	20	271	7.2	2.3	42.5	1.3	2.5	0.22	183	91	35	c
5-HA	100	263	14.1	4.6	45.7	1.3	8.6	0.47	182	71	37	c
6-HA	200	263	20.5	6.6	46.9	1.4	6.7	0.44	188	91	36	c
Humic-Acid Stock Solution	330	297	1.3	0.05	45.9	1.4	3.6	0.53	229	110	32	3.69

	Constituent, mg/L									
	Cr	Cu	Mn	Ni	Sr	Ti	V	Zn	Zr	
1-HA	0.023	<0.010	0.008	<0.020	0.019	<0.010	<0.020	0.016	<0.010	
2-HA	0.023	<0.010	0.008	<0.020	0.018	<0.010	<0.020	0.013	<0.010	
3-HA	0.027	0.019	0.010	0.020	0.020	<0.010	<0.020	0.014	<0.010	
4-HA	0.032	0.014	0.013	0.020	0.021	<0.010	<0.020	<0.010	<0.010	
5-HA	0.081	0.033	0.028	0.043	0.039	0.032	<0.020	0.020	0.020	
6-HA	0.142	0.038	0.040	0.070	0.055	0.049	<0.020	0.020	0.029	
Humic-Acid Stock Solution	0.021	0.020	<0.005	<0.020	<0.005	0.087	<0.020	0.061	0.025	

(contd)

Table 5 (Contd)

Test-Solution Number ^a	Humic-Acid DOC, mg/L	Constituent, mg/L										
		Na	Ca	Mg	Si	B	Fe	Al	Cl ⁻	SO ₄ ⁻²	F ⁻	Alkalinity ^b
After Reaction at 90°C												
1-HA	0	275	5.0	0.7	73.9	8.2	0.13	0.23	184	116	35	c
2-HA	1	259	3.4	0.6	76.7	7.8	0.37	0.37	189	107	35	c
3-HA	10	269	4.4	0.7	74.1	7.5	0.94	0.36	183	100	34	c
4-HA	20	265	5.6	1.1	70.4	5.8	1.5	0.42	182	107	34	c
5-HA	100	295	15.3	4.8	66.3	2.0	1.9	0.38	190	118	35	c
6-HA	200	269	20.4	8.8	69.6	2.1	3.4	0.43	182	107	33	c

	Constituent, mg/L								
	Cr	Cu	Mn	Ni	Sr	Ti	V	Zn	Zr
1-HA	0.022	<0.010	<0.005	0.021	0.020	<0.010	0.032	0.011	<0.010
2-HA	0.027	<0.010	0.006	0.025	0.012	<0.010	0.038	0.011	<0.010
3-HA	0.032	0.015	0.010	0.032	0.015	0.012	0.038	0.017	0.011
4-HA	0.035	0.025	0.014	0.036	0.018	0.022	0.039	0.015	0.013
5-HA	0.080	0.078	0.040	0.078	0.047	0.030	0.050	0.017	0.016
6-HA	0.131	0.100	0.100	0.150	0.063	0.035	0.053	0.032	0.025

^aOriginal notebook designation of these test solutions is 239-45.

^bAlkalinity of these solutions, in units of milliequivalents, is due to the ions CO₃⁻², HCO₃⁻, H₂BO₃⁻, H₃SiO₄⁻, and OH⁻.

^cSample of insufficient size for measurement.

IV. EFFECTS OF HUMIC ACID ON NUCLIDE PARTITIONING IN SYNTHETIC GROUNDWATER

A. Americium Partitioning

1. Variable pH Groundwater

Initial solution pH was determined by the concentration of humic acid in the solution; it ranged from 9.92 at zero level of total DOC to 8.79 at a concentration level of 200 mg/L (Table 2). No attempt was made in these experiments to adjust the initial pH of the test solutions to a uniform value.

The results of reacting the test solutions with crushed basalt for seven days at ambient temperature (22°C) and at 90°C are given in Table 6. As the distribution ratio (R_d) values indicate, both the temperature of the reaction and the concentration of DOC in solution have pronounced effects on sorption of americium by the crushed basalt. Sorption of americium is increased by one to two orders of magnitude, at all concentration levels of humic acid used in the tests, by an increase in temperature of the reaction from 22°C to 90°C. By contrast, R_d values display a decrease of one to two orders of magnitude with increase in humic-acid DOC from zero to 200 mg/L in both the 22°C and 90°C experiments. The concentration of only 1 mg/L DOC, compared to the zero concentration, exhibited a decrease in R_d values of about 50% at both temperatures.

Figure 1 illustrates the effects of both increased temperature and increased concentration of DOC. Note the marked difference in R_d values calculated from the samples reacted at 22°C and 90°C, and the sharp drop in R_d values with increased concentrations of humic-acid DOC, particularly in the samples reacted at 90°C.

2. pH-Adjusted Groundwater

Because of the possibility that the sorption trends described in these experiments could have been caused by changes in solution pH rather than by complexing with the humic acid, an additional experiment was run with solutions identical to those used in the experiments above except that solution pH was adjusted to a uniform value before the experiments began. All solutions were adjusted to a pH of 9.92 ± 0.01 by addition of small increments of 0.0968N NaOH, as shown in Table 7. The solutions were then spiked with americium, placed in the test vials with granulated basalt, and allowed to react for seven days at 22°C and 90°C in the same manner described for the experiments with variable pH.

The results of this experiment are given in Table 8 and Fig. 2. The R_d values for americium shown here are higher than those reported in Table 6; however, the trend of decreasing R_d values with increasing concentration of DOC in the solutions is the same. Compared to the zero concentration, the R_d values decrease by 10% to 40% at the humic-acid DOC concentration of 1 mg/L and by one to two orders of magnitude at 200 mg/L. The same trend of increasing R_d with increasing temperature of the reaction was observed, although the effects of temperature are less pronounced compared to those in the experiment with variable pH solutions.

Table 6. Results of Batch Partitioning Experiments with Americium and Humic Acid in Variable pH Groundwater. [Distribution ratio was measured in experiments using granulated (60-80 mesh) Pomona basalt reacted in synthetic groundwater containing various concentrations of humic-acid DOC. Initial pH of each solution is shown in Table 2.]

Test-Solution Number ^a	Humic-Acid DOC, mg/L	Distribution Ratio (R _d), ^b mL/g
<u>Experiment at 22°C</u>		
1-HA (1-3)	0	10.0 (1.5) ^c
2-HA (7-9)	1	4.7 (0.6)
3-HA (13-15)	10	4.9 (0.2)
4-HA (19-21)	20	3.3 (0.2)
5-HA (25-27)	100	2.9 (0.6)
6-HA (31-33)	200	1.9 (0.8) ^c
<u>Experiment at 90°C</u>		
1-HA (4-6)	0	245 (64) ^c
2-HA (10-12)	1	132 (32)
3-HA (16-18)	10	68 (21)
4-HA (22-24)	20	28 (3.5)
5-HA (28-30)	100	9 (1.5)
6-HA (34-36)	200	8 (0.5) ^c

^a Parenthetical entries indicate original replicate designations.

^b Arithmetic mean of distribution ratios calculated from triplicate runs. Standard deviation of the mean is given in parentheses.

^c The R_d values measured in the presence of zero and 200 mg/L added DOC were found to be different using the t-statistic compared to Student's t distribution, at a confidence level greater than 99%, for data at both 22°C and 90°C.

Fig. 1. Average Distribution Ratio, R_d , for Americium as a Function of Concentration Level of Humic Acid Reacted at 22°C and 90°C with Granulated Pomona Basalt, pH Not Adjusted

Table 7. Adjustment of pH of Test Solutions Using 0.0968N NaOH

Test-Solution Number	Humic-Acid DOC, mg/L	Initial pH	Amount of NaOH Added, mL	Adjusted pH
1-HA	0	9.91	0	9.91
2-HA	1	9.86	0.121	9.93
3-HA	10	9.84	0.098	9.92
4-HA	20	9.83	0.132	9.93
5-HA	100	9.45	0.467	9.91
6-HA	200	8.67	0.821	9.91

Table 8. Results of Batch Partitioning Experiments with Americium and Humic Acid in pH-Adjusted Groundwater. [Distribution ratio was measured in experiments using granulated (60-80 mesh) Pomona basalt reacted in synthetic groundwater containing various concentrations of humic-acid DOC. Initial pH of all solutions was adjusted to 9.2.]

Test-Solution Number ^a	Humic-Acid DOC, mg/L	Distribution Ratio (R_d), ^b mL/g	Remarks
<u>Experiment at 22°C</u>			
1-HA (221-223)	0	94 (9) ^c	
2-HA (227-229)	1	85 (30)	
3-HA (233)	10	69 -	Single run
4-HA (239-241)	20	33 (6)	
5-HA (245-247)	100	4.9 (3.1)	
6-HA (251-253)	200	2.9 (1.1) ^c	
<u>Experiment at 90°C</u>			
1-HA (224-226)	0	475 (200) ^d	
2-HA (230-232)	1	217 (30)	
3-HA (236-238)	10	68 (18)	
4-HA (242-243)	20	40 (21)	Duplicate run
5-HA (248-250)	100	6.5 (0.6) ^d	
6-HA (255-256)	200	2.3 (0.6)	Duplicate run

^a Parenthetical entries indicate original replicate designations.

^b Arithmetic mean of distribution ratios calculated from triplicate runs, except as indicated. Standard deviation of the mean is given in parentheses.

^c The R_d values measured in the presence of zero and 200 mg/L added DOC were found to be different using the t-statistic compared to Student's t distribution, at a confidence level greater than 99%.

^d The R_d values measured in the presence of zero and 100 mg/L added DOC were found to be different using the t-statistic compared to Student's t distribution, at a 95% confidence level.

Fig. 2. Average Distribution Ratio, R_d , for Americium as a Function of Concentration Level of Humic Acid Reacted at 22°C and 90°C with Granulated Pomona Basalt, Initial pH Adjusted to 9.2

These results support the conclusion that the variations in sorption behavior of americium observed in the first experiments are caused primarily by complexing of americium in the presence of different concentrations of humic acid, rather than by differences in initial pH of the test solutions. Furthermore, decrease in pH from 9.92 in the test solution with a zero level of DOC to 8.79 in the solution with a DOC concentration of 200 mg/L should produce an increase in sorption of americium, according to the data of [ALJARD]. The fact that the opposite trend is actually observed in the experiments is consistent with the interpretation that the changes in sorption are caused primarily by the complexing effect of the organic carbon in solution.

B. Neptunium Partitioning

Batch partitioning experiments were conducted with neptunium to determine whether or not variations in the concentration of dissolved humic acid affected the sorption of neptunium in a manner similar to that observed with americium. Test solutions having 0, 1, 10, 20, 100, and 200 mg/L humic-acid DOC were prepared by the same processes discussed in the americium experiments, spiked with neptunium, and allowed to react with crushed basalt for seven days at 22°C and 90°C. Solution pH was not adjusted.

The effects of humic-acid DOC concentration on sorption of ^{237}Np onto basalt are summarized in Table 9 and Fig. 3. Distribution ratios (R_d) for neptunium are considerably lower than the values for americium at comparable

Table 9. Results of Batch Partitioning Experiments with Neptunium and Humic Acid. [Distribution ratio was measured in experiments using granulated (60-80 mesh) Pomona basalt reacted in synthetic groundwater containing various concentrations of humic-acid DOC.]

Test-Solution Number ^a	Humic-Acid DOC, mg/L	Distribution Ratio (R_d), ^b mL/g	Remarks
<u>Experiment at 22°C</u>			
1-HA (37-39)	0	8.0 (3.2) ^c	
2-HA (40-42)	1	6.1 (2.0)	
3-HA (43-45)	10	4.2 (0.3)	
4-HA (46-48)	20	4.5 (0.3)	
5-HA (49-51)	100	1.4 (0.2)	
6-HA (52-54)	200	1.3 (0.1) ^c	
<u>Experiment at 90°C</u>			
1-HA (55-57)	0	28 (4) ^d	
2-HA (58-60)	1	20 (1)	
3-HA (61-63)	10	13 (1)	
4-HA (64-66)	20	10 (3)	
5-HA (67-69)	100	3.5 (0.4) ^d	
6-HA (70,72)	200	2.4 (0.3)	Duplicate run

^a Parenthetical entries indicate original replicate designations.

^b Arithmetic mean of distribution ratios calculated from triplicate runs, except as indicated. Standard deviation of the mean is given in parentheses.

^c The R_d values measured in the presence of zero and 200 mg/L added DOC were found to be different using the t-statistic compared to Student's t distribution, at a 93% confidence level.

^d The R_d values measured in the presence of zero and 100 mg/L added DOC were found to be different using the t-statistic compared to Student's t distribution, at a 99% confidence level.

Fig. 3. Average Distribution Ratio, R_d , for Neptunium as a Function of Concentration Level of Humic Acid Reacted at 22°C and 90°C with Granulated Pomona Basalt

concentrations of DOC; however, the same trend of decreasing R_d values with increasing concentration of organic carbon is evident. Increase in DOC from zero to 200 mg/L caused a progressive decrease in R_d from about 28 to 2 mL/g in the 90°C experiment and from 8 to 1 mL/g in the 22°C experiment. At a concentration of only 1 mg/L of humic-acid DOC, R_d values decreased by about 25%. The trend of increasing nuclide adsorption with increasing temperature established in the americium experiments was also observed in the neptunium experiment. Samples reacted at 90°C show distribution ratios about three times greater than those reacted at 22°C at all concentration levels of DOC tested.

V. EFFECTS OF FULVIC ACID ON NUCLIDE PARTITIONING IN SYNTHETIC GROUNDWATER

A. Introduction

Because the humic substances in natural groundwaters may contain as much as 85% fulvic acid [THURMAN], we wished to determine whether the presence of fulvic acid in synthetic groundwater produced a comparable effect on nuclide adsorption to that observed with humic acid. Test solutions containing 0, 1, 10, 20, 100, and 200 mg/L fulvic-acid DOC were prepared from a stock solution of fulvic acid containing 400 mg/L DOC, as described in Section II.A.2. Americium and neptunium were added to separate batches of these solutions during the preparation process. Batch partitioning experiments with crushed basalt were carried out under the same conditions and by the same processes used in the experiments with humic acid (Sec. IV).

B. Americium Partitioning

The results of batch partitioning experiments conducted for seven days with fulvic acid and americium are summarized in Table 10 and Fig. 4. These results show trends of increased sorption of americium with increasing temperature and decreased sorption with increasing concentration of fulvic-acid

Table 10. Results of Batch Partitioning Experiments with Americium and Fulvic Acid. [Distribution ratio was measured in experiments using granulated (60-80 mesh) Pomona basalt reacted in synthetic groundwater containing various concentrations of fulvic-acid DOC.]

Test-Solution Number ^a	Fulvic-Acid DOC, mg/L	Distribution Ratio (R_d), ^b mL/g
<u>Experiment at 22°C</u>		
1-FA (185-187)	0	18 (0) ^c
2-FA (188-190)	1	23 (3)
3-FA (191-193)	10	12 (3)
4-FA (194-196)	20	11 (3)
5-FA (197-199)	100	3.3 (0.6)
6-FA (200-202)	200	2.7 (0.6) ^c
<u>Experiment at 90°C</u>		
1-FA (203-205)	0	562 (58) ^c
2-FA (206-208)	1	278 (0)
3-FA (209-211)	10	86 (6)
4-FA (212-214)	20	43 (3)
5-FA (215-217)	100	16 (4)
6-FA (218-220)	200	20 (8) ^c

^a Parenthetical entries indicate original replicate designations.

^b Arithmetic mean of distribution ratios calculated from triplicate runs. Standard deviation of the mean is given in parentheses.

^c The R_d values measured in the presence of zero and 200 mg/L added DOC were found to be different using the t-statistic compared to Student's t distribution, at a confidence level greater than 99%, for data at both 22°C and 90°C.

Fig. 4. Average Distribution Ratio, R_d , for Americium as a Function of Concentration Level of Fulvic Acid Reacted at 22°C and 90°C with Granulated Pomona Basalt

DOC; the trends are quite similar to those observed in the experiments with americium and humic acid. Distribution ratios (R_d) calculated from samples reacted at 90°C range from a mean value of 562 mL/g at zero level of DOC to a mean value of 20 mL/g at a concentration of 200 mg/L, a difference of more than an order of magnitude. The concentration of 1 mg/L of fulvic-acid DOC, compared to the zero concentration, exhibited a decrease in R_d values of about 50%.

Samples reacted at 22°C yielded distribution ratios that are lower by an order of magnitude than those determined at 90°C and comparable concentrations of DOC. At 22°C, values of R_d range from a mean of 18 mL/g at zero DOC to a mean of 3 mL/g at a fulvic-acid DOC concentration of 200 mg/L, different by a factor of six. In this experiment, a concentration of 1 mg/L of DOC, with respect to zero concentration, indicated an apparent increase in R_d values of about 20% rather than a decrease. The reason for this one anomalous value is not clear and may be due to experimental error.

C. Neptunium Partitioning

The results of partitioning experiments conducted for seven days with fulvic acid and neptunium are shown in Table 11 and Fig. 5. These results are similar to those found with ^{241}Am and fulvic acid, although R_d values for neptunium at comparable temperatures and DOC concentrations tend to be

Table 11. Results of Batch Partitioning Experiments with Neptunium and Fulvic Acid. [Distribution ratio was measured in experiments using granulated (60-80 mesh) Pomona basalt reacted in synthetic groundwater containing various concentrations of fulvic-acid DOC.]

Test-Solution Number ^a	Fulvic-Acid DOC, mg/L	Distribution Ratio (R_d), ^b mL/g	Remarks
<u>Experiment at 22°C</u>			
1-FA (221-223)	0	19 (12) ^c	
2-FA (224-226)	1	8.7 (1)	
3-FA (227-228)	10	6.8 (1)	Duplicate run
4-FA (230-232)	20	8.7 (1)	
5-FA (233-235)	100	2.1 (0.3)	
6-FA (236-238)	200	1.7 (0.4) ^c	
<u>Experiment at 90°C</u>			
1-FA (239-241)	0	49 (6) ^d	
2-FA (242)	1	51 -	Single run
3-FA (245-247)	10	40 (5)	
4-FA (248-250)	20	48 (9)	
5-FA (251-253)	100	12 (3)	
6-FA (254-255)	200	8 (2) ^d	Duplicate run

^aParenthetical entries indicate original replicate designations.

^bArithmetic mean of distribution ratios calculated from triplicate runs, except as indicated. Standard deviation of the mean is given in parentheses.

^cThe R_d values measured in the presence of zero and 200 mg/L added DOC were found to be different using the t-statistic compared to Student's t distribution, at a confidence level of 87%.

^dThe R_d values measured in the presence of zero and 200 mg/L added DOC were found to be different using the t-statistic compared to Student's t distribution, at a confidence level of 99%.

Fig. 5. Average Distribution Ratio, R_d , for Neptunium as a Function of Concentration Level of Fulvic Acid Reacted at 22°C and 90°C with Granulated Pomona Basalt

somewhat lower. The means of R_d values determined at 90°C range from 49 at zero level of DOC to 8 at a concentration of 200 mg/L fulvic-acid DOC, somewhat less than an order of magnitude difference. In this experiment at 90°C, the concentration of 1 mg/L of fulvic-acid DOC exhibited no detectable change in R_d values from those at zero concentration.

The means of R_d values determined at 22°C range from about 20 mL/g at zero level of DOC to 1.7 mL/g at a concentration of 200 mg/L fulvic-acid DOC. The concentration of 1 mg/L fulvic-acid DOC, compared to the zero concentration, showed a decrease in R_d values of about 45%. The general trend of R_d values decreasing with increasing concentration of DOC is interrupted for unknown reasons between 10 and 20 mg/L; that is, values obtained at concentrations of 20 mg/L are somewhat higher than those at 10 mg/L.

VI. DISCUSSION

The radioactive solutions used in this work were prepared by adding an acid spike of americium to the groundwater or by dissolving a neptunium salt into the groundwater. The concentrations of americium prepared in this manner were $9 \times 10^{-10}M$ or lower. These prepared concentrations are below the solubility limit for americium in groundwater similar in composition to that used in these experiments, predicted to be $1.4 \times 10^{-8}M$ from calculations by [EARLY]. This suggests that the americium was unaffected by precipitation reaction and that the predominant process that led to the removal of americium from solutions was surface reaction.

The concentrations of neptunium were $\sim 3.6 \times 10^{-6}M$ or lower in the prepared solution. The concentrations used experimentally are below the solubility limit calculated for neptunium in groundwater similar to that used experimentally (standard oxidation-reduction potential above 0.0 V) [EARLY]. This suggests that precipitation may have been an important process in removing neptunium from solution, because a reduction of neptunium (from the +5 valence state to the +4 valence state) would lead to a solubility limit below the concentrations used experimentally. Reduction of neptunium by basalt has been reported [MEYER]. In addition, organic acids such as those used in these experiments are known to be capable of reducing neptunium from the +5 state to the +4 state [NASH]. This suggests that neptunium removal from solution in these experiments could have involved precipitation as well as sorption on rock surfaces and complexation with organic molecules. The extent to which the organic acids increase the solubility of neptunium is not known at this time, but may be sufficient to prevent precipitation even if the reduction of neptunium does occur. In any case, the ability of organic acids to enhance the amount of neptunium that remains in solution on contact with basalt is clear from these experiments. In this manner, both americium and neptunium are affected similarly by organic acids, in spite of large differences in the details of their chemical behaviors.

The organic acids used in this work were purified chemically to remove some complexing metals and ash. In some ways, the organic acids investigated experimentally are chemically more reactive than organic acids in groundwaters that remain complexed with commonly occurring metals. Substantial chemical reactivity is noted, for example, by the enhanced dissolution of Ca, Mg, Fe, Mn, Ni, and Sr from basalt by solutions that contain 20 mg/L or more of purified dissolved organic carbon. Although the results of the experiments clearly establish the characteristics of organic acid reactions with americium and neptunium, the distinction between organic acids prepared in the laboratory and those occurring naturally should be recognized before results of these experiments are used to predict behavior in a natural environment.

Americium and neptunium were chosen for study because they have long-lived isotopes that are components of nuclear waste. Although both elements are expected to hydrolize and to form carbonate complexes at the pH of 8 to 10 used in the experiments, the elements are otherwise chemically very different. Americium exhibits a single valence state, +3, in aqueous solutions such as those used here, whereas neptunium may exist in the +3, +4, and +5 valence states. Neptunium +5 would be expected to be the predominant species under oxidizing conditions. But in the presence of organic materials and the ferrous ion in basalt [EARLY], much of the neptunium could be reduced to the +4 state. The reduced neptunium species are known to be less soluble and more strongly sorbed onto rock surfaces than the oxidized species [MEYER].

Sorption of both americium and neptunium onto rock surfaces is known to be pH sensitive, with nuclide adsorption generally increasing with increases in pH [SERNE]. In the case of americium, sorption is reported to be strongly influenced by increase in pH at values between 4 and 6, but shows a slight decrease with increasing pH values above 6 [ALLARD]. This slight decrease with increasing pH values was not evident in the results of the experiments reported here.

This work used crushed basalt as the sorbent and gives results of direct relevance to repository performance, because new rock fissures will be introduced in the construction of a nuclear waste repository by the mining operation and by backfilling of excavations with crushed basalt. Also important to understanding the potential for nuclide migration is the sorption of americium and neptunium on rock surfaces altered over time such as those indigenous to the rock surrounding the excavation. In the future, sorption on altered rock surfaces will be studied using granulated rock altered hydrothermally in the laboratory and naturally fissured rock sampled directly from the formation.

The experimental temperatures of 22°C and 90°C span temperatures typically encountered in some deep rock structures. For example, the ambient temperatures of the Umtanum flow in the Columbia River basalts at the location considered for nuclear waste disposal is 58°C. Elevated temperatures near 90°C could occur in the flow due to heating from radioactive decay of emplaced waste. Lower temperatures would be encountered away from the repository and nearer the surface of the ground.

Columbia River basalts, of which the Pomona flow studied in this work is a member, have limited ranges of chemical, mineralogical, and physical characteristics. The basalts are distinguishable from one another. For example, in terms of magnesium content, high-magnesium basalts such as the Pomona flow contain ~7.0 wt % MgO; low-magnesium basalts contain 3.6 wt % MgO, with a range of >1 wt % (3.3% to 4.4%) experienced in individual flows such as Umtanum. Therefore, on chemical and mineralogical bases, the Pomona flow is typical of the high-magnesium basalt we need to know about in terms of nuclide migration.

The characteristics of nuclide transport in the Pomona basalt are nuclear waste disposal issues because the basalt occurs at a depth of 250 m at the reference location for the disposal of nuclear waste [ROCKWELL]. Inasmuch as nuclear waste would be disposed of at depths below 900 m, the Pomona basalt lies between the proposed repository and the surface of the accessible environment.

VII. SUMMARY AND CONCLUSIONS

Batch partitioning experiments with americium and neptunium in synthetic groundwaters containing dissolved humic or fulvic acid show that sorption of americium and neptunium onto granulated basalt is strongly influenced by the concentrations of these organic acids. Experiments were conducted at both 22°C and 90°C to explore the influence of temperature on sorption in the presence of organic acids. At 22°C, radionuclide sorption, as measured by distribution ratios (the ratio of nuclide sorbed onto the solid to nuclide in solution at the end of the experiment), decreases by about 25% to 50% by addition of as little as 1 mg/L dissolved humic or fulvic acid organic carbon. Addition of progressively higher concentrations of these acids causes a correspondingly greater decrease in sorption, with distribution ratios decreasing up to one to two orders of magnitude at dissolved organic carbon concentrations of 100-200 mg/L. Similar, but less pronounced, effects of the humic and fulvic acids were seen in the experiment at 90°C.

This trend of decreasing sorption with increasing concentration of dissolved organic carbon was observed both in experiments in which the initial pH of humic-acid groundwater solutions was adjusted to a uniform value (9.2) and in experiments in which the initial pH existed in the range of 8.8 to 9.9 due to the different concentrations of humic acid in the groundwater. The experiments with and without pH adjustment were run at 22°C and 90°C. The suppressing effects of dissolved organic carbon on nuclide adsorption appear clearly to be caused by complexing of the radionuclides with the organic carbon and not by ancillary changes in pH produced by the presence of different concentrations of organic acids.

Partitioning experiments carried out at different temperatures show that temperature has a pronounced effect on sorption of americium and neptunium. Experiments run at 90°C yielded distribution ratios ranging up to one to two orders of magnitude greater than in identical experiments carried out at ambient temperature (22°C), showing that sorption of americium and neptunium is greatly enhanced at the higher temperature.

The main conclusion that emerges from this study of the effects of organic complexing on radionuclide sorption is that dissolved humic and fulvic acids artificially introduced into synthetic groundwaters complex readily with americium and neptunium. Such complexing suggests that these elements would have significantly increased mobility in a groundwater-rock environment where organic acids are present. On the other hand, increased temperature of the groundwater enhances sorption and, hence, decreases the mobility of the elements americium and neptunium. Although the results reported here using synthetic groundwaters dosed with humic and fulvic acid are useful in estimating the effects of organic acids on element behavior, the results cannot necessarily be extrapolated to natural groundwater systems. Clearly, additional studies of natural groundwaters must be made to establish more definitively the effects of indigenous dissolved organic carbon and metallic ions on mobility of actinide elements before these results can be applied to the specific problems of siting high-level radioactive waste repositories.

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