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SORPTION OF AMERICIUM IN TUFF AND PURE MINERALS USING SYNTHETIC AND NATURAL GROUNDWATERS

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The distribution of Am between selected solid and liquid phases has been studied using initial ^{241}Am solutions with a molarity smaller than 1×10^{-11} . The synthetic and natural groundwaters used have pH values in the 7-8 range and a total alkalinity of approximately 1 mN which is mainly due to bicarbonate. Mass spectrometric isotope dilution was utilized to determine the amount of Am in the solution phase initially and after equilibrium was attained. Using this sensitive technique, 7×10^8 atoms of ^{241}Am were accurately measured. Our results indicate that the percent of Am lost to the walls of the container in the absence of geologic material varies from 35 to 84. The Am sorption coefficient determined is on the order of 10^3 ml/g for clinoptilolite, 10^4 ml/g for tuff consisting mainly of alkali feldspar and cristobalite, and 10^5 ml/g for romanechite.

KEYWORDS: Americium, Sorption, Groundwater, Tuff, Clinoptilolite, Romanechite

INTRODUCTION

The sorption behavior of Am in geologic and non-geologic media has been studied using natural and synthetic groundwaters. Mass spectrometric isotope dilution analysis was utilized to determine the amount of ^{241}Am in the initial solution and in the solution at equilibrium with the selected solid phases. This sensitive analytical technique allowed the utilization of Am concentrations smaller than the lowest value published¹⁻³ for the thermodynamic solubility of Am. The results obtained in this study can be utilized for the prediction of migration behavior of actinides in the proposed high-level nuclear waste repository at Yucca Mountain, NV.

Previous results¹ indicate that the Am is trivalent under environmental conditions. Carbonate complexes like AmCO_3^+ and $\text{Am}(\text{CO}_3)_2^-$ are the dominating species in solution. The Am solubility has been reported² to have a minimum of about $10^7 - 10^8$ M in the pH range from 7-9. The solubility limiting solid phase is $\text{Am}_2(\text{CO}_3)_3$ in the environmental pH range.

Kerrisk³ has studied the solubility of Am in water from the J-13 well of the Nevada Test Site. The J-13 groundwater is believed to be representative of the water at the site of the proposed repository in Yucca Mountain. The chemistry of this groundwater has been reported.^{4,5} The J-13 water has an alkalinity of 2 mN. The reported³ Am solubility

in J-13 water is greater than 10^{-9} M in the pH range from 7.5-8.0. At these pH values, AmCO_3^+ is the predominant species in solution, the percent of $\text{Am}(\text{CO}_3)_2^-$ relative to the total Am present is from 10 to 20 and the hydrolysis products AmOH^{+2} and $\text{Am}(\text{OH})_2^+$ are less than 10%.

The mechanisms for the sorption of actinides have been reviewed.² Physical adsorption, electrostatic adsorption (ion exchange), and chemisorption have been observed for actinide sorption in aqueous environmental systems. Americium is reported to sorb strongly in the pH range from 7 to 8 due to physical adsorption. The sorption of Am in minerals of igneous rocks has been studied^{6,7} using synthetic groundwater. The molarity of Am in the initial solutions used for the sorption studies in igneous rocks was 2×10^{-9} . The measured sorption⁶ in terms of distribution coefficients was $4-7 \times 10^3$ ml/g for granite and $2-6 \times 10^3$ ml/g for basalt.

EXPERIMENTAL

Cleanup Procedure of Glassware and Teflon Containers

The teflon and glassware utilized for sorption experiments was thoroughly cleaned. The glass and teflon equipment utilized for experiments involving solution #1 (from Table 1) was heated in 50% HNO_3 overnight, thoroughly rinsed with Milli-Q H_2O (water with a resistivity greater than 16 mega-ohms), and air dried in a clean air hood.

For experiments involving solutions #2 and #3 (from Table 1) the cleaning procedure involved: a) soaking glassware and teflon containers in Isoterge soap for one day, b) rinsing the equipment with Milli-Q water multiple times, c) cleaning equipment with a 1:1 HCl to Milli-Q water solution by soaking the equipment in the solution, applying low heat for a minimum of one day, boiling for one hour, cooling and decanting the solution, and rinsing the equipment with Milli-Q water, d) repeating step c using Aqua Regia (3:1 HCl to HNO_3), e) repeating step c using a 1:1 HNO_3 to Milli-Q water solution, f) repeating step c using Milli-Q water with a trace of HNO_3 , and g) air-drying the equipment in a class-100 air clean room.

Preparation and Analysis of Am Feed Solutions

The method of preparation for the three Am initial or feed solutions that were equilibrated with the selected solid phases are described in Table 1. Solution #1 was prepared by taking an aliquot of an acidic $^{241}\text{Am}(\text{III})$ stock solution to dryness and redissolving the Am in J-13 water.

Solutions #2 and #3 were prepared by dilution of an ^{241}Am stock solution with J-13 water and pH 7.5 buffer, respectively. The stock solution of Am in the +3 oxidation

state was filtered through a 0.05 micrometer filter before dilution was effected. The stock solution had an original Am molarity of 1.3×10^{-7} . Liquid scintillation counting was utilized to determine the amount of Am lost during filtration; only 5% of the Am was lost during filtration through the 0.05 micrometer filter.

The sodium carbonate - sodium bicarbonate buffer utilized for solution #3 was prepared to obtain a pH of 8.6 and an alkalinity of 1.2×10^{-3} N. The ultra pure water utilized for preparation of this buffer solution was obtained by sub-boiling point distillation of Milli-Q water in a class-100 air clean room. The pH measured for the buffer solution prepared was 7.5. The reason for this unexpectedly low pH value is that all the glassware and teflon containers utilized for preparation of the buffer and distillation of the Milli-Q water were cleaned with acid solutions (as previously discussed). Although all glassware and teflon containers were thoroughly rinsed with Milli-Q water after each step in the acid clean up procedure, the amount of rinsing was not sufficient to leach the acid from the walls of the containers used.

Solutions #2 and #3 were prepared and left in pyrex glass volumetric flasks for 20 days. After 20 days the solutions were shaken and liquid scintillation counting was utilized to determine the amount of Am lost to the walls of the volumetric flasks. Solution #2 lost 79% of the original amount of Am to the glass walls of the flask in 20 days; solution #3 only lost 9%. Consequently, a fresh batch of solution #2 was prepared for the sorption experiments.

The molarity of the feed solutions used is given in Table 1. These Am concentrations were determined by mass spectrometric isotope dilution. Aliquots of solution #1-3 were traced with a known amount of ^{243}Am . A chemical procedure⁸ was utilized to clean the samples in order to recover only the ^{241}Am and ^{243}Am in the traced aliquots. The ratios of ^{241}Am to ^{243}Am were measured by mass spectrometry. These ratios allowed the determination of the amount of ^{241}Am in the feed solutions.

Characterization and Preparation of Minerals

Tuff sample GU3-688 was obtained from drill hole USW GU-3 at Yucca Mountain, NV at a depth of 688 feet. Tuff GU3-688 and romanechite from Casa Grande, AZ were ground and sieved. Particles in the size range from 75-500 μm were used for the sorption experiments. Ground clinoptilolite from Castle Creek, ID was purchased and purified using the method of Chipera and Bish.⁹

Quantitative X-ray diffraction analysis was performed on the tuff¹⁰ and minerals. Tuff GU3-688 is 68% alkali feldspar, 27% cristobalite, 4% quartz and 1% smectite. No impurities were detected in the romanechite sample. The purified clinoptilolite was 98% pure; the

other 2% consists of smectite and quartz.

Romanechite is a manganese oxyhydroxide mineral with chemical formula $\text{BaMn}^{+2}\text{Mn}_8^{+4}\text{O}_{16}(\text{OH})_2$. Clinoptilolite is a zeolite mineral. Zeolites are hydrous aluminosilicates, analogous in composition to feldspars. Zeolites are powerful ion exchangers, their ratio of Al plus Si to nonhydrous oxygen is 1:2. The chemical formula of clinoptilolite is $\text{M}_8\text{Al}_8\text{Si}_{28}\text{O}_{72}\cdot 24\text{H}_2\text{O}$, where M is mostly K. The moles of Al per gram of zeolite determines the equivalents of metal cations that can potentially exchange with one gram of the exchanger. In the case of clinoptilolite the exchange capacity is approximately 1 milliequivalent per gram.

Pre-sorption Equilibration of Solid Phase with Groundwater

The solid phases studied (teflon, GU3-688, romanechite, and clinoptilolite) were pre-treated by contact with the groundwaters specified in Table 2 for a period of time varying from 1 to 36 days. Table 2 shows the contact times for the pre-sorption equilibration.

The pre-sorption step consists of shaking the samples containing both phases for the specified contact time and separating the phases by centrifugation. The solution to solid ratio utilized in the pre-sorption step for the tuff and minerals is 100 ml to 1 g. In the absence of geologic materials 100 ml of the appropriate groundwater were added to the teflon containers.

Phase separation for the experiments using feed solution #1 for the sorption step was effected by centrifuging the samples at 5,000 rpm for one hour and pipetting out the supernatant. Centrifugation using feed solutions #2 and #3 in the sorption step was effected at 3,000 rpm.

Sorption Equilibration of Solid Phases with Am Solution

Aliquots of the Am feed solutions specified in Table 2 were added to the solid phases which had been previously equilibrated with the appropriate groundwaters. The samples containing the solutions and solid phases were shaken for 21 days. For samples containing geologic material, the solution to solid ratio utilized is 100 ml to 1 g. In the absence of geologic material, 100 ml of the appropriate Am feed solution were added to the teflon container. Teflon bottles were utilized for the Am sorption experiments using tuff and minerals. Separation of phases for the sorption step involved ultracentrifugation.

Phase separation of the samples using feed solution #1 for the sorption step involved: a) taking an aliquot of 70 ml of the equilibrated Am solution and centrifuging for one hour at 30,000 rpm, b) taking an aliquot of 60 ml from the supernatant in step a and centrifuging for one hour at 30,000 rpm, and c) taking an aliquot of 50 ml of the supernatant in step b and centrifuging for two hours at 30,000 rpm.

For samples using feed solutions #2 and #3 for the sorption step, phase separation

involved: a) centrifuging the samples after sorption equilibration for one hour at 3,000 rpm, b) taking an aliquot of 60 ml of the supernatant in step a and centrifuging for one hour at 30,000 rpm, and c) taking an aliquot of 50 ml of the supernatant in step b and centrifuging for two hours at 30,000 rpm.

The portions of Am solution remaining after each centrifugation step were combined for pH determinations. The Am left in the solution phase after equilibration was determined by analyzing an aliquot of the supernatant from the last centrifugation step using mass spectrometry.

RESULTS AND DISCUSSION

The results from the sorption of Am onto the walls of the teflon containers using different feed solutions are summarized in Table 3. Losses of 35% to 84% of the Am during equilibration of the feed solution with non-geologic media indicates that physical adsorption² due to non-specific forces of attraction between the solid and the sorbing Am is an important mechanism for sorption of actinides.

The definition of K_d is given in Equation 1.

$$K_d = \frac{\text{moles of Am in solid phase/g of solid}}{\text{moles of Am in solution phase/ml of solution}}, \text{ at equilibrium} \quad (1)$$

The sorption coefficients K_d reported in Table 4 for GU3-688, romanechite, and clinoptilolite were determined by difference. The moles of Am in the solid phase, at equilibrium, are assumed to be equal to the moles of Am in the aliquot of feed solution added to the solid minus the moles of Am present in the equilibrated solution phase. In the case of romanechite, mass spectrometry was able to precisely measure 7×10^8 ²⁴¹Am atoms left in the solution phase after equilibration.

The assumption that equilibrium is attained in 21 days between the solid and the solution phase for the sorption of Am is inherent in the definition of K_d . There is no evidence to prove or disprove this assumption. If equilibrium was not attained in the sorption steps of these experiments, the value of the K_d 's reported should be used as distribution coefficients for Am between the solid and solution phases given the set of conditions stated in the experimental section.

Although the sorption of Am by the walls of the teflon container is evident, no correction for this adsorption was made in the calculation of K_d 's for geologic material. Previous results¹¹ indicate that the sorption of Am on container walls is negligible in the presence of the large active surface areas provided by crushed tuff and minerals.

The results presented in Table 4 agree with previous results.¹² Although the sorption of Am was not previously studied in GU3-688, tuff GU3-433 was used for Am sorption

studies. Tuff sample GU3-433 from drill hole USW GU3 (Yucca Mountain, NV) at a depth of 433 feet does not differ much in composition from GU3-688. Tuff GU3-433¹⁰ is 76% alkali feldspar, 15% cristobalite, 2% mica, and 1% hematite. The sorption coefficient reported¹² is approximately 3×10^4 ml/g using an Am feed solution in J-13 water of 2×10^{-7} M. This K_d is of the same order of magnitude as the one reported in Table 4 for GU3-688. The Am sorption coefficient value reported¹² for tuff sample G4-1502 is 2×10^3 ml/g using an Am feed solution in J-13 water of 1×10^{-8} M. Tuff G4-1502¹⁰ from drill hole USW G-4 (Yucca Mountain, NV) at 1502 feet depth has a composition of 71% clinoptilolite, 15% Opal-CT, 4% quartz, 3% alkali feldspar and 2% smectite. Tuff G4-1502 is similar in composition to the purified clinoptilolite sample used in the present studies. The Am K_d measured for the purified clinoptilolite is of the same order of magnitude as the one reported for G4-1502.

The agreement between previous¹² and current results seems to indicate that the sorption coefficients reported using Am feed solutions between 10^{-7} and 10^{-8} M were not the result of precipitation. The K_d obtained for clinoptilolite could be the result of ion exchange. Although the value obtained (10^3 ml/g) is smaller than the value expected for a strong cation exchanger, the small K_d could be due to the large size of AmCO_3^+ . It is conceivable that this large cation does not fit into the cages of clinoptilolite normally occupied by small resident cations such as K^+ . The large K_d measured for romanechite could be due to chemisorption driven by the formation of complexes between species in the solid surface and Am species in solution. However, the results presented do not provide conclusive evidence for either of these two mechanisms (ion exchange or chemisorption). In fact, considering the current and previously reported^{2,6,12} data, physical adsorption remains the most obvious mechanism to explain Am sorption. The only problem with the latter sorption mechanism is that the nature of the Am solution species undergoing physical adsorption is not clear. The data obtained for loss of Am in glass and teflon seem to support the existence of a colloidal Am species suspended in solution.

SUMMARY

The sorption of Am was studied using ^{241}Am feed solutions with a molarity of less than 10^{-11} . This concentration is smaller than the published values for the thermodynamic solubility of Am. Consequently, the sorption results obtained are not likely a result of precipitation. The synthetic and natural groundwaters used for the sorption experiments have a pH in the range from 7 to 8, the total alkalinity is on the order of 1 mN. The Am in the feed solution and in the solution equilibrated with the selected solid phase was determined by mass spectrometric isotope dilution. The percent of Am lost during

equilibration of Am feed solutions with the walls of the teflon containers varied from 35 to 84. These results indicate that Am can undergo sorption by physical adsorption. The sorption coefficients calculated were determined by difference (the Am in the solid phase, at equilibrium, was determined by analyzing the solution phase before and after equilibration). The sorption coefficient measured was on the order of 10^3 ml/g for clinoptilolite, 10^4 ml/g for tuff GU3-688, and 10^5 ml/g for romanechite. Analysis of the current and previous results indicates that physical adsorption remains the most obvious mechanism to explain Am sorption.

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Table 1: Concentration of Am Feed Solution

Feed Solution No.	Method of Preparation	Molarity		
		Trial 1	Trial 2	Average
1	Taking an aliquot of Am stock solution to dryness; Redissolving Am in J-13 groundwater	7.1×10^{-12}	6.7×10^{-12}	6.9×10^{-12}
2	Diluting an aliquot of Am stock solution in J-13 groundwater	5.8×10^{-12}	5.1×10^{-12}	5.5×10^{-12}
3	Diluting an aliquot of Am stock solution in pH 7.5 buffer solution	5.9×10^{-12}	6.1×10^{-12}	6.0×10^{-12}

Table 2: Amount of Time of Equilibration for Pre-sorption and Sorption Steps

Sorptive Material	Groundwater utilized for Pre-Sorption	Am Solution utilized for Sorption Step*	Time of Equilibration (Days)			
			Pre-Sorption		Sorption	
			Trial 1	Trial 2	Trial 1	Trial 2
Teflon	J-13	1	1	1	21	21
Teflon	J-13	2	36	15	21	21
Teflon	pH 7.5 Buffer	3	15	15	21	21
GU3-688	J-13	1	1	1	21	21
Romanechite	pH 7.5 Buffer	3	36	36	21	21
Clinoptilolite	pH 7.5 Buffer	3	15	36	21	21

*From Table 1

Table 3: Equilibration of Feed Solutions with Walls of Teflon Containers

Feed Solution No.*	Molarity after Equilibration			% Lost to Walls of Teflon Container	pH of Feed Solution after Equilibration
	Trial 1	Trial 2	Average		
1	4.3×10^{-12}	4.7×10^{-12}	4.5×10^{-12}	35	
2	2.0×10^{-12}	2.4×10^{-12}	2.2×10^{-12}	60	7.5
3	1.1×10^{-12}	8.0×10^{-13}	9.5×10^{-13}	84	7.4

*From Table 1

Table 4: Sorption Coefficients for Am

Solid Phase	Feed Solution Utilized*	Kd (ml/g)			pH of Solution Phase at Equilibrium
		Trial 1	Trial 2	Average	
GU3-688	1	1.4×10^4	9.5×10^3	1.2×10^4	
Romanechite	3	3.2×10^5	3.3×10^5	3.3×10^5	8.0
Clinoptilolite	3	4.0×10^3	5.7×10^3	4.9×10^3	8.2

*From Table 1