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Informal Report

MASTER

Sorption-Desorption Studies on Granite

I. Initial Studies of Strontium, Technetium, Cesium, Barium, Cerium, Europium, Uranium, Plutonium, and Americium

University of California

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I. Initial Studies of Strontium, Technetium, Cesium, Barium, Cerium, Europium, Uranium, Plutonium, and Americium

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SORPTION-DESORPTION STUDIES ON GRANITE

I. Initial Studies of Strontium, Technetium, Cesium, Barium, Cerium, Europium, Uranium, Plutonium,and Americium

by

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ABSTRACT

Distribution ratios were determined for sorption-desorption of radioactive tracers between the Climax Stock granite (quartz monzonite porphyry) obtained at Nevada Test Site and a water prepared to be resonably representative of the natural composition of water in equilibrium with the Climax Stock granite. The measurements were performed at 22°C and 70°C under atmospheric oxygen conditions. Elements given in order of increasing distribution coefficient at at ambient temperature are: U(VI), Sr, Tc(VII), Ba, Ce(III), Cs, Eu(III), Pu, and Am. At 70°C the order is: Tc(VII), Sr, Ce(III), Eu(III), Ba, Cs, Pu, and Am. The effects of surface area and mineralogy on sorption were also investigated.

SUMMARY

The most important barrier to the movement of dissolved radionuclides in geologic systems is retardation due to the interaction between the radionuclides and the geologic medium. This report summarizes the first investigations on the behavior of various radionuclides using granite from the Climax Stock area at the Neveda Test Site (NTS).

A batch technique has been developed for all sorption and desorption measurements. One gram quantities of the crushed and sieved rock were pre-equilibrated for a minimum of two weeks with a water having a composition similar to a natural water. The spiked water was prepared by a similar *pre-equilibration with ground but unsieved material. The evaporated radionuclides were then dissolved in this pre-equilibrated water. Twenty-mℓ portions of the spiked water were shaken with the pre-equilibrated rock for various contact times, the mixture was separated by four separate centrifugations at 16 000 rpm, and the solution was assayed for radioactivity. Due to the removal of some radionuclides by the container in which the measurements were performed, it was necessary to sample all or part of the solid fraction in order to obtain accurate values. Techniques and calculational methods were developed for this purpose. The residue from the sorption measurements were employed for the desorption experiments using the same technique.*

Various particle sizes ranging from 106 to 850 µm, and both ambient and elevated (70°C) temperatures were used. Changes in the sorption-desorption behavior with time were examined for intervals of 1, 2, 4, and 8 weeks. The elements studied were Sr, Tc(VII), Cs, Ba, Ce(III), Eu(III), U(VI), Pu, and Am. The measurements were performed under atmospheric oxygen conditions.

The sorption ratio (R_d = activity per g of solid/activity per mℓ of water) increases slowly with time presumably due to the slow interaction of the rock surface with the groundwater. Surface alterations presumably are also the reasons for the observation that it is more difficult to remove Cs, Ce, Eu, Pu, and Am from the rock than it was to sorb these elements (desorption ratio greater than sorption ratio). The sorption ratios for all elements studies, except Ce and Eu, scale with surface area or particle size and increase with temperature. This presumably indicates that Ce and Eu do not follow an ion-exchange or sorption mechanism. No appreciable sorption of Tc(VII) and U(VI) was observed.

Permeability and porosity measurements were also made on consolidated cores.

I. INTRODUCTION

A major requirement for the evaluation of the long term safety of nuclear waste disposal in a geologic storage environment is a thorough understanding of the mechanisms and phenomenology of the sorption-desorption behavior of the various radionuclides that are biologically hazardous. Hopefully this knowledge will aid in the prediction of the fate of the radionuclides during the length of time required for radioactive decay to reduce the waste to safe levels.

This report presents the results of laboratory investigations of the sorption behavior of various radionuclides with the Climax Stock granite (quartz monzonite porphyry) found at the Nevada Test Site (NTS). The investigation was intended to satisfy two functions. First, specific information was needed in order to help make a decision as to the feasibility of using granite as a waste repository medium. Second, this work provides input to the large general database of sorption information needed for a variety of representative geologic media.[1]

The parameter most commonly used for describing equilibrium sorption-desorption ion-exchange reactions is the distribution coefficient, K_d (see, for example, Ref. 2). The K_d is defined as the concentration per gram of a species on a solid phase divided by its concentration per ml in the liquid phase at equilibrium. This parameter currently is being used to describe the behavior of radionuclides in geologic systems, (see, for example, Refs. 1, 3, and 4) even though equilibrium may not have been established.

II. GEOLOGIC MATERIAL PROPERTIES

A. Mineralogy

Two different samples of the Climax Stock granite (labelled CS5 and CS7, respectively) were obtained from the mine dump area of the Piledriver tunnel at the Nevada Test Site (NTS). Thin-sections of this material were prepared and examined by optical microscopy to determine grain size, original mineralogy, and alteration phases. The following were observed:[5]

Major minerals	*Approx. Average Grain Diameter*
Quartz - strained, cracked, fairly interlocking with plagioclase	*0.6 mm*
Plagioclase - very strongly concentrically zoned, minor myrekite	*0.4 mm*
K-feldspar - microcline phenocrysts (very large), orthoclase in matrix	*0.4 mm*
Biotite - discrete flakes	
Opaques, including sulfides	

Minor minerals

Sphene, zircon, apatite, and tourmaline

Alteration

Sericite and probable clay in plagioclass
Epidote
Chlorite in biotite
Calcite, very minor

The outer layers from the two pieces of granite were removed with hammers, and the remaining material (about 5 lbs. each) was reduced in size with hammers, with a Braun Chipmunk apparatus, and finally with a pulverizer having the plates set at ∿ 1 mm. Each material was graded by use of Tyler sieves (ASTM E-11 specification) into the following size fractions: $>$ 850 μm, 500-850 μm, 355-500 μm, 250-355 μm, 180-250 μm, 150-180 μm, 106-150 μm, and $<$ 106 μm.

The 106 -150 μm, 250-355 μm,and 500-850 μm fractions were selected for subsequent use in the sorption studies. The fractions were washed briefly with deionized water to remove dust. They were then dried in air, pumped in a sealed vacuum desiccator containing Drierite for one hour, and dried in the desiccator for two days. The petrographic (modal analysis) description[6] of these fractions is given in Tables I and II.

B. Cation Exchange Capacity

The cation exchange capacity (CEC) of each of the three fractions selected for study was measured using both cesium and strontium. The measurement was made[7] by shaking weighed 100-mg portions of the solids with 20 mℓ of ~ 0.5 M

TABLE I
VOLUME PERCENT IN CS5 FRACTIONS

	Mesh Size (μm)		
	106-150	250-355	500-850
Quartz	31	29	24
Feldspar[a]	48	58	61
Altered feldspar[b]	2	4	5
Biotite, chlorite	10	7	7
Sphene	< 1	1	1
Apatite	< 1	< 1	< 1
Opaques[c]	8	1	1

---

[a] Contains clay-rich alteration
[b] Two feldspars present in about equal proportion: plagioclase, K-feldspar
[c] Magnetite plus ilmenite

TABLE II
VOLUME PERCENT IN CS7 FRACTIONS

	Mesh Size (μm)		
	106-150	250-355	500-850
Quartz	40	32	26
Feldspar[a]	46	54	60
Altered feldspar[b]	2	7	5
Biotite + Chlorite	5	6	8
Sphene	2	2	< 1
Apatite	< 1	< 1	< 1
Opaques[c]	5	1	< 1

---

[a] Contains clay-rich alteration
[b] Two feldspars present in about equal proportions: plagioclase, K-feldspar
[c] Magnetite plus ilmenite

CsCl (pH = 8.2) or ~ 0.5 M $SrAc_2$ (pH = 8.5) in deionized water for 8-14 days. The solutions were spiked with ^{137}Cs and ^{85}Sr, respectively, and the cation concentrations were determined by atomic absorption spectrophotometry. After the appropriate contact time the phases were separated by centrifugation, the solids were washed with water and were counted with a NaI(Tl) detector to ascertain the amount of strontium or cesium that had exchanged. The results from these measurements are given in Table III. As expected for granite, the values are all very low. However, the CEC determined using strontium was generally higher than that obtained using cesium.

TABLE III

CATION EXCHANGE CAPACITY AND SIEVE ANALYSIS

		Cation Exchange Capacity		Particle Size Distributions (μm)		
Sample	Mesh Size (μm)	Cs	Sr	Range	Median	Semi-inter-Quartile Range
CS5	106-150	< 1	1	106-210	132	12
CS5	250-355	< 1	< 1	180-500	300	30
CS5	500-850	< 1	1	425-1000	688	81
CS7	106-150	< 1	2	106-250	133	11
CS7	250-355	< 1	2	180-500	293	30
CS7	500-850	< 1	3	425-1000	690	86

C. Size Distribution Analysis

The size distributions of the particles in the three selected fractions were measured by screening techniques.[8] For the range data, the sizes of the smallest screens through which 100% of the material passed were not recorded. However, the screen size listed in Table III as the upper bound for each sample is the size immediately larger than the size recorded as having collected the largest particles in a sample. The median values in Table III were calculated by linear interpolation between screen size data that immediately bracketed the median mass. Similarly, the upper and lower quartile values were calculated by linear interpolation between the screen data that immediately bracketed the 75% and 25% mass values, respectively. The semi-interquartile range as defined by Cramer[9] is a measure of the dispersion of the particle size distribution.

D. Surface Area

The surface area of the fractions has been determined by two different techniques, the BET method[10] and the ethylene glycol method.[11-13] The values are summarized in Table IV. The BET method employed nitrogen as the adsorbate.[8] A fraction of ground and pulverized Climax Stock granite from another location at the Piledriver site at the NTS was also used as an intercomparison of BET values determined at the Los Alamos Scientific Laboratory (LASL), Sandia Laboratories (SLA),[14] and the Lawrence Livermore Laboratory (LLL).[15] SLA used krypton as the absorbate. The values were 0.20, 0.27, and 0.31 m^2/g, respectively. The agreement is satisfactory considering the rather low values.

Briefly, the equilibrium ethylene glycol procedure[10,11] consists of wetting a dried and weighed sample of calcium saturated material with glycol. This is then followed by equilibration in an evacuated desiccator containing an anhydrous calcium chloride - ethylene glycol solvate. The equilibration is repeated until the weights become constant, presumably indicating that only a monolayer remains. The results obtained using the standard procedure are shown in the fourth column of Table IV.

TABLE IV
SURFACE AREA (m^2/g) MEASUREMENTS

Sample	Mesh Size (μm)	BET	Ethylene Glycol $CaCl_2$ Pretreatment	Ethylene Glycol No $CaCl_2$ Pretreatment
CS5	106-150	0.95	8.0	1.3
CS5	250-355	0.16	4.0	4.4
CS5	500-850	0.10	7.0	2.9
CS7	106-150	0.80	9.0	4.5
CS7	250-355	0.16	3.3	3.6
CS7	500-850	0.12	3.0	2.8

The equilibrium ethylene glycol method[11,12] requires that the samples be saturated with calcium prior to treatment with the glycol. This is needed in order to make the systems homoionic.[13] However, since the clay content of the granites is expected to be low, the surface areas were also determined without this pretreatment. This was also done to see if the prior treatment had degraded the samples. These data (see Table IV) would seem to indicate that the pretreatment is not necessary for granite samples.

E. Permeability

The permeability of a core sample (labelled 2b) of the material from the same area as those described earlier was measured using the apparatus depicted in Fig. 1. The sample was ground to the form of a right circular cylinder, 2.54 cm in diameter by 1.6 cm long. The sample was placed in a Teflon sleeve and a porous disc of pressed stainless steel fiber was placed on both ends of the sample. Steel cylinders of the same diameter as the sample with pressure lines attached were then inserted into the ends of the Teflon cylinder and the whole assembly was placed in a pressure vessel. The system was pressurized and allowed to stabilize with the upper and lower pore pressure lines at the same pressure. The pressure in the lower pore pressure line was then decreased. After disappearance of the initial transient effects (approximately 1 min), the pressure difference between the upper and lower pore pressure lines was measured at 1 second intervals for 30 to 60 seconds. These readings were then fit to an equation of the form $\Delta P = \Delta P^\circ e^{-\alpha t}$, where ΔP° is the pore pressure difference at the beginning of the measuring interval, α is[16]

$$\alpha = (kA/\mu\beta L)(1/V_1+1/V_2)$$

k is the permeability, A is the cross-sectional area, L is the length of the sample, μ is the viscosity, β the compressibility of the fluid, V_1 is the volume of the upper pore pressure line, and V_2 is the volume of the lower pore pressure line.

Measurements can be made over a pore pressure range of 0-14 MPa and confining pressure range of 0-40 MPa. The upper limit of the temperature range of the measurements is limited to about 473 K by the stability of the Teflon parts.

The permeability was measured at 296, 326, 397, and 463 K as a function of the effective confining pressure (confining pressure minus pore pressure) from 1 to 10 MPa. The measured permeabilities range from 10^{-18} to 10^{-21} m^2. The permeability generally decreases slightly with increasing temperature. However, at the higher effective confining pressures permeabilities at 463 K are slightly higher than at 397 K. The permeability as a function of temperature and effective confining pressure is given in Figs. 2-5.

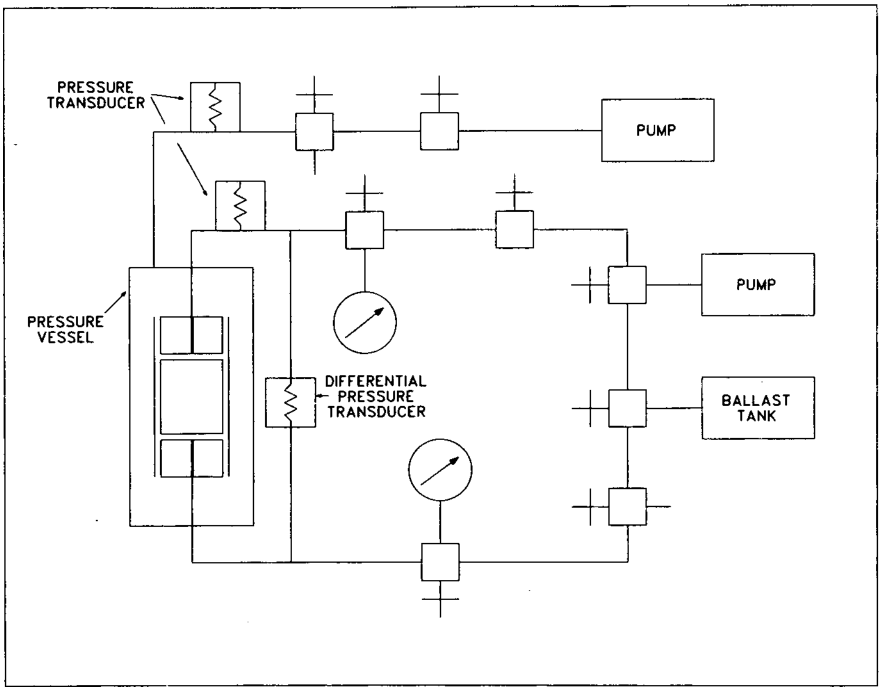

Fig. 1. Schematic of the permeability apparatus.

At effective confining pressures above 10 MPa the permeability was generally below the measuring range of the apparatus (about 10^{-21} m^2). At permeabilities lower than 10^{-21} m^2 the pressure decay was so slow that it was obscured by pressure changes caused by temperature fluctuations in the apparatus.

F. Porosity

The effective porosity of another core sample of Climax Stock granite (designated 6A) obtained from the mine dump area was measured using an apparatus based on the device for measuring permeability developed by Brace et al.[16] as modified by Potter.[17] It is quite similar to that shown in Fig. 1 and described in Section II.E, except that the liquid at only one end of the core is pressurized, while that at the other, exit, end is at atmospheric pressure. Liquid leaving the rock passes through a 0.048-cm i.d. stainless steel tube to a collecting vessel.

Effective (connected pore space) porosity was measured by first utilizing the pressure system to saturate the rock with tritiated water of known specific

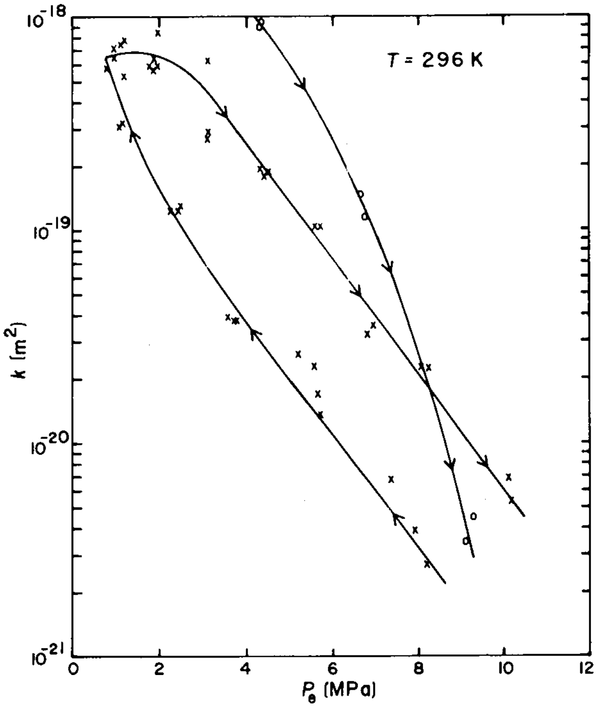

Fig. 2. Permeability measurements at 296 K as a function of confining pressure.

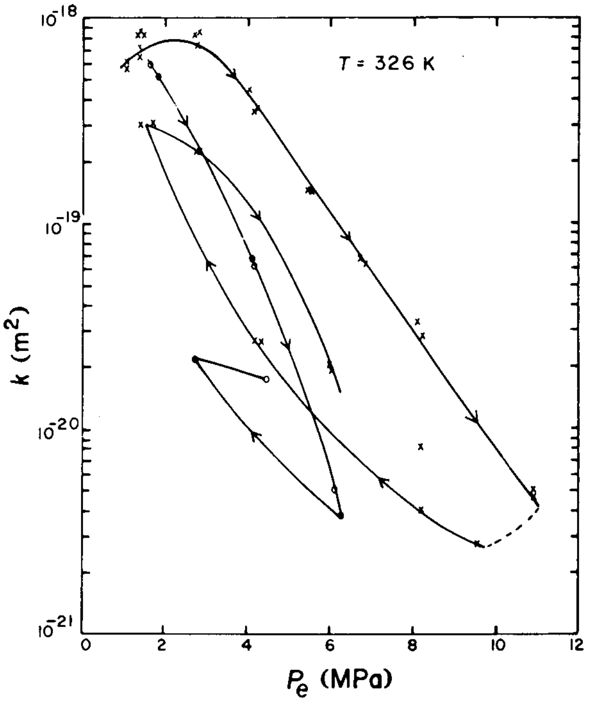

Fig. 3. Permeability measurements at 326 K as a function of confining pressure.

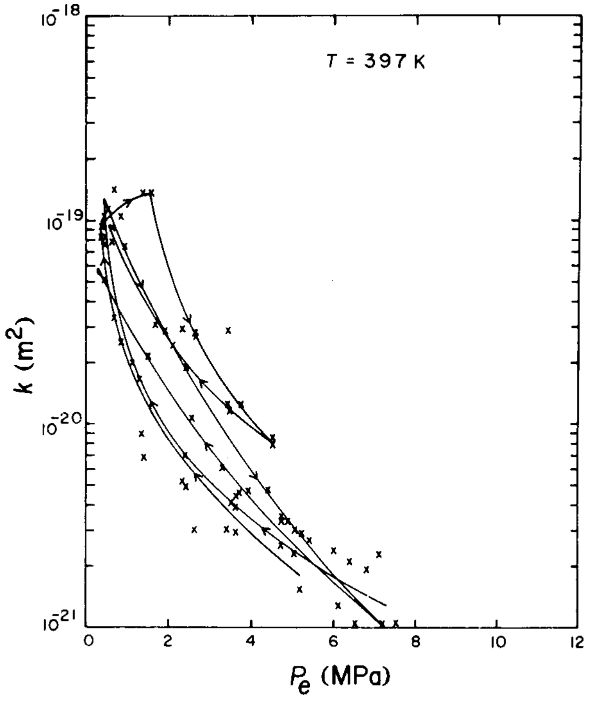

Fig. 4. Permeability measurements at 397 K as a function of confining pressure.

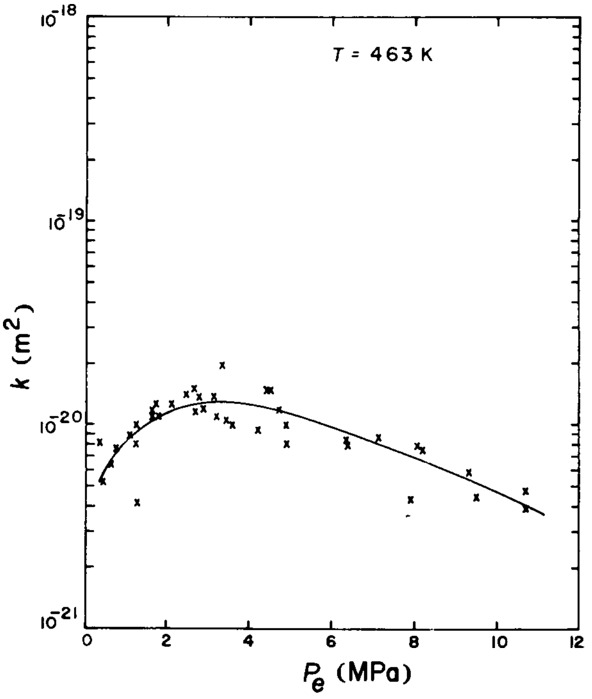

Fig. 5. Permeability measurements at 463 K as a function confining pressure.

activity. The core was removed, and the system was purged with water until the wash showed no tritium activity. The core was returned to the line and flushed with water until the tritium dropped essentially to zero. The total amount of tritium removed is a measure of the volume of tritiated water contained at saturation. The effective porosity is then the ratio of the volume of tritiated water, i.e., pore space, and the total volume of the core. This method of porosity measurement is quite useful for low porosities since the specific activity of the tritiated water can be increased as required.

Porosities measured by this technique are probably essentially at atmospheric pressure. Although pressures as high as 5 MPa are used to force liquid through the cores, the exit end is at atmospheric pressure and the rock is surrounded by tritiated water at the time the applied pressure is released. The core would tend to "inhale" tritiated water as it relaxes.

The Climax granite core was found to have a porosity of $\approx 0.15\%$ based on a single measurement which will be repeated. For comparison, the porosities[18] of two Los Alamos Geothermal Site cores of quartz monzonite measured by this technique were found to be 0.45% and 0.50%.

G. Ground Water Properties

When the studies discussed in this report were begun no natural ground water representative of the Climax Stock granite system was available. Therefore a "synthetic" water was used. The composition of the water was taken from the report of Feth et al.[19] (See Table V.) This composition is the mean value from selected perennial springs from granodiorite in the Sierra Nevada. The water was made by adding 1.3 mℓ KCl solution (1.72 mg/mℓ), 1.3 mℓ NaCl solution (7.30 mg/mℓ), 1.3 mℓ Na_2SO_4 solution (23.9 mg/mℓ), 17.1 mℓ 0.1 N NaOH to 123 mg $Ca(OH)_2$ and 29.0 mg H_2SiO_3. The mixture was then diluted to 8.0 ℓ with deionized water, followed by sparging with carbon dioxide for at least 12 h. After sparging the solution with nitrogen until a pH of ~ 8 was reached, it was allowed to air-equilibrate for at least one week prior to use. The typical atmospheric pressure at Los Alamos is ~ 580 mm Hg.

Rock pre-equilibrated water was used in all the sorption measurements given in this report. This was prepared by contacting batches of the "synthetic" water with ground material that had not been sieved. The contact time was at least two weeks with a solution volume to solid water ratio of 20 mℓ/g.

TABLE V

ANALYSIS OF WATERS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

(mg/ℓ)

Constituent	Ref. 19	Lab[a]	Batch 1		Batch 2		Batch 3		Batch 4	
			22°C	70°C	22°C	70°C	22°C	70°C	22°C	70°C
Ca	8.3	8.36	8.7	9.5	10.0	9.7	9.3	9.4	9.1	8.7
K	1.5	1.6	4.9	3.7	3.7	3.3	2.9	3.0	3.6	3.0
Mg	1.5	1.5	1.6	0.20	2.2	0.42	1.5	0.68	2.1	0.53
Na	6.7	6.2	5.0	5.9	5.8	6.3	6.0	6.0	6.6	6.4
Si	12.5	13.6			12.9	15.3		16.1	13.6	15.3
SO_4	2.7									
Cl	2.1									

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[a] Water before equilibration

The phases were separated by centrifugation at 7 000 rpm followed by filtration through a 0.45 μm Nuclepore filter paper. This procedure was used for preparation of waters pre-equilibrated at ambient temperature (22 ± 2°C) and at elevated temperature (70 ± 1°C). The same rock phase with fresh "synthetic" water was used to prepare all subsequent batches. Table V summarizes the results of atomic absorption spectrophotometric analysis of these waters. Selected batches of these waters were also sent to the U. S. Geological Survey for analysis, and the results[20] are given in Table VI. Only the calcium and potassium concentrations at both temperatures are appreciably different than the "synthetic" water. In addition, the potassium concentration seems to decrease with continued equilibration. The pH of each of these waters was also measured using glass and standard reference electrodes.

III. SORPTION OF STRONTIUM, CESIUM, BARIUM, CERIUM, AND EUROPIUM

A. Measurement Techniques

1. Preparation of Tagged Solutions

All traced waters used in these studies were prepared using the pre-quilibrated waters described previously and the following commercially available carrier-free or high specific activity radionuclides: ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, and ^{152}Eu. The concentrations for these tracers are given in Table VII. The specific activities given are those provided by the manufacturer. The activities (μCi/mℓ) were measured on a calibrated Ge(Li) detector system (see below). The element concentrations given in Table VII only include that consciously added with the tracer. The appropriate volumes of tracers needed for a set of measurements were evaporated to dryness in a washed polyethylene tube overnight on a steam bath. Concentrated hydrochloric acid was added, and the mixture was taken dry again in order to convert the salts to chlorides. The appropriate volume of pre-equilibrated ground water was added, and the mixture was stirred for ~ 24 hrs. The mixture was centrifuged for one hour at 16 000 rpm, followed by filtration through a 0.45 μm Nuclepore filter paper. The resulting tracer solution was used for the sorption measurements within about 0.5 day. An aliquot of the final solution was also removed for assay of the initial activity of each of the tracers in the solution. This aliquot was acidified with hydrochloric acid before assaying in order to stabilize the solution. During the tracer preparation no cesium, strontium or barium were lost, but about 50% of the cerium and europium was lost onto the filter paper.

TABLE VI
USGS[20] WATER ANALYSES

	Batch 1		Batch 4
	22°C	70°C	22°C
		(mg/ℓ)	
Barium (Ba)	0.3	0.3	0.3
Calcium (Ca)	9.6	11	11
Iron (Fe)	0.4	0.07	0.09
Lithium (Li)	0.03	0.02	0.02
Magnesium (Mg)	2.0	0.2	2.0
Potassium (K)	4.8	3.7	2.9
Silicon (Si)	7.9	12	10
Sodium (Na)	7.5	8.6	7.7
Strontium (Sr)	0.07	0.09	0.03
Bicarbonate (HCO_3)	55	49	57
Carbonate (CO_3)	0	0	0
Chloride (Cl)	2.3	2.5	2.3
Fluoride (F)	0.3	0.1	0.1
Sulfate (SO_4)	5.1	6.5	3.9
		(meg/ℓ)	
Total Cations	1.093	1.034	1.123
Total Anions	1.088	1.014	1.086

TABLE VII

ELEMENT CONCENTRATIONS

	Tracer		Traced Water	
	Specific Activity (mCi/g)[a]	Activity (μCi/mℓ)	Tracer Concentration (μl/mℓ)	Element Concentration (molar)
^{85}Sr	300	21	1.5	1.2×10^{-6}
^{137}Cs	CF	34	0.5	1.4×10^{-9}
^{133}Ba	8120	51	0.3	2.4×10^{-8}
^{141}Ce	600	110	1.	1.3×10^{-6}
^{152}Eu	2638	32	1.	8.0×10^{-8}

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[a] CF means carrier-free

One should note that the pre-equilibrated water itself may have considerable concentration of the carriers for each of these tracers. This concentration will be measured in the future when neutron activation analyses are made on each of the batches of water used in this study.

2. Sorption Measurements

Batch sorption experiments were performed by shaking weighed one gram quantities of the crushed rock with 20 mℓ untraced pre-equilibrated water for a period of two weeks. The three selected were fractions from each of the two cores (CS5 and CS7) and were used for the studies at ambient (22 ± 2°C) temperature, while only those fractions from CS7 were used for the measurements at elevated temperature (70 ± 1°C). The samples were contained in stoppered 40 mℓ polyethylene centrifuge tubes at ambient temperature or in sealed polypropylene tubes at elevated temperature. All tubes were washed with deionized water prior to use. The phases were separated by centrifuging at 16 000 rpm for one hour. The weight of the wash solution remaining with the solid phase was obtained by weighing the tube and solid before and after the pre-equilibration. A 20-mℓ volume of the tagged pre-equilibrated water was then added to the tube, the solid sample was dispersed with vigorous shaking, and the mixture was agitated gently for a given time. Typically, 1, 2, 4, and 8 week contact times were used. The shaking rates were 200 oscillations per minute of the ambient temperature studies and 80 oscillations per minute for the 70°C samples. A water bath shaker was used for the latter studies. At the end of the shaking period, the aqueous phase was separated from the solids by four centrifugings, each in a new polyethylene centrifuge tube, for one hour at 16 000 rpm. An aliquot of the final solution was then removed and placed in a standard scintillation counting polyvial. This solution was acidified with hydrochloric acid, and it was then assayed for the remaining activities. The pH of the solutions before and after contact with the rock was also recorded.

All solutions remaining from the sorption measurements, including the solution used for radioactivity assay, have been stored for future measurement of the final concentration of the major cations in these solutions. These analyses are to be performed using a multichannel direct reading emission spectrograph utilizing a direct current argon-plasma excitation source. The procedures for these analyses are currently being developed on a Spectrometrics, Inc., model 3 spectrograph.

The same sorption procedure was also performed using a tube that did not have a solid phase present. This control sample was used to indicate if any of the radionuclides were likely to be removed by the container. In all cases (see below), the strontium, cesium, and barium remained completely in solution. However, not all of the cerium and europium remained in solution. It was felt that the amount of sorption on the container would vary, depending on whether or not solid material is present, since elements appear to adsorb on any available surface. Therefore, the presence of a solid phase would tend to reduce the fraction of the activity adsorbed on the container. This effect would be especially large when crushed rock solid phase are used since they have an appreciable surface area (see Table IV).

In order to determine the amount of activity remaining with the solid phase, whether due to sorption, precipitation, centrifugation of a colloid with the solid, or by some other mechanism, a fraction (~ 25%) of the solid was removed for radioactivity assay. The solid phase was well mixed prior to sample removal. The fraction of the solid removed was determined from the activity of ^{137}Cs in the solid aliquot, in the solution, and in the initial solution. This method is reasonable since cesium did not adsorb on the container walls. A check was made by weighing the tube before and after removing the sample. Of course, the limitation in this method is how representative the fraction is of the entire solid.

3. Desorption Measurements

Desorption measurements were made for all samples previously used for the sorption measurements, except for the eight week sorption samples. The assay of the activity on the solid was done as described earlier. A 15 mℓ volume of untagged pre-equilibrated water was used for each measurement in order to keep the volume to solid ratio ~ 20. Contact times of 2, 4, and 8 weeks were used for the 4, 2, and 1 week sorption measurement samples. The same procedure was used for separation of the phases and for radioactivity assay as was used in the sorption measurements. This includes the assay of the radioactivity on a fraction of the solid material.

4. Assay of Radioactivity

The solution samples were all counted on a calibrated, 14%, coaxial Ge(Li) detector. An 11% Ge(Li) detector system was used for the solid fractions. The two different detector systems were carefully intercalibrated. The 4096 channel spectra were recorded in multichannel analyzers,which are connected to a common PDP-9 computer, where they were analyzed on-line by RAYGUN, our in-house gamma-ray spectroscopy program.[21] This program is designed for use on a minicomputer and it includes spectral interpretation. Its operation involves: 1) a search for background and peak (nonbackground) regions; 2) a preliminary peak search in the nonbackground regions; 3) construction of a step function under the peak(s) in each region; 4) construction of an underlying continuum by smoothing the background together with the step functions; 5) a search for peak regions and peaks with stricter criteria; 6) determination of peak positions and areas, and correction for photopeak efficiency; if a multiplet is encountered, separation of the peaks by using peak shape information; 7) a search of the appropriate gamma-ray branching ratio library to find those nuclides and gamma-rays that appear to be in the spectrum, eliminating those that are not plausible. 8) set up an interference matrix, $[A_{ij}]$, where A_{ij} = branching ratio for the i^{th} peak identified corresponding to the j^{th} nuclide identified; 9) by a least-squares iteration determine a solution to

$$Y_i = \sum_j A_{ij} X_j \ (X_j \text{ unknown}),$$

where Y_i = observed intensity of the i^{th} peak and x_j = disintegration rate for the j^{th} nuclide; 10) correction of the disintegration rate observed for each radionuclide at the counting time to a specified time; 11) performance of an error analysis and output of the results in suitable form. A minimum of two counts, separated by at least one day, were taken for each sample. The results from the RAYGUN analyses for each count were simply averaged prior to use.

5. Calculations

The equilibrium distribution coefficient, K_d, for the distribution of activity between the two phases is conventionally defined as:

$$K_d = \frac{\text{activity in solid phase per unit mass of solid}}{\text{activity in solution per unit volume of solution}} .$$

It is not known whether equilibrium is achieved for the types of measurements reported here. However, the distribution of activities between the phases is measured, and throughout this report the resulting value is called the sorption ratio, R_d, which is otherwise identical to K_d, but does not imply equilibrium.

The following equation was used to calculate the sorption ratios for strontium, cesium,and barium:

$$R_d = \frac{R \cdot A_f - A_t}{A_t} \cdot \frac{V}{W} \quad . \qquad (1)$$

where

A_f = the activity per mℓ of a given radionuclide in the tagged water (feed) added to the sample

A_t = the activity per mℓ in the supernatant solution after the required contact time

W = the weight (grams) of solid material used

V = the total final volume of supernatant solution

R = the dilution factor to take into account the residual solution from the wash that remains with the solid.

The amount of residual solution (V_r) left with the solid material was calculated from the weight increase of the sample plus container (g_r) after the two prewashes, and the measured density (ρ_r) of the solutions used:

$$V_r = g_r / \rho_r .$$

Therefore, for these measurements (20.0 mℓ spike volume)

$$V = 20.0 + V_r$$

and

$$R = 20.0 / (20.0 + V_r) .$$

The activities in the control samples were not used in the calculations. However, the results would not be changed since no container effect was observed in these experiments.

The standard deviation for each measurement was obtained from the errors associated with the activity measurements (generally less than 2%), 3% uncertainty assumed for g_r, a 0.5 mg uncertainty in W, and a 0.5% uncertainty in the volumes. The errors were propagated using the rule for change of variables in a moment matrix assuming independence of the variables and Eq. (1).

For the cerium and europium cases, a different calculational method was used. Since a container problem has never been observed for cesium, the sorption ratio for cesium was used as an internal monitor. The activity of cerium/europium and cesium in the solid and solution samples was measured. Since the sorption ratio is

$$R_d = \frac{A_s}{A_t} \cdot \frac{V}{W} , \qquad (2)$$

where

$$A_s = \text{activity on the solid,}$$

then if a ratio of R_d values is calculated using Eq. (2) one has, after rearrangement,

$$R_{dx} = \frac{\left(\dfrac{A_{sx}}{A_{sm}}\right)}{\left(\dfrac{A_{tx}}{A_{tm}}\right)} R_{dm} , \qquad (3)$$

where the x and m refer to the cerium/europium and cesium, respectively. This equation was used to calculate the sorption ratio for the cerium/europium since the R_d for cesium was calculated using Eq.(1)in the same experiment.

The standard deviation was calculated using the same procedure as previously discussed and Eq.(3).

For the desorption measurements the sorption ratio was again calculated assuming that the cesium did not have an affinity for the container. The activity, A^o_{sm}, of ^{137}Cs on the solid at the beginning of a desorption measurement was calculated using

$$A^o_{sm} = A^o_m \ (1-f) \ (1-f_d) ,$$

where

A^o_m = the initial ^{137}Cs activity at the beginning of the sorption measurement

f_m = the fraction of ^{137}Cs activity remaining solution after the sorption measurement

f_d = the fraction of the solid removed from the sample prior to beginning the desorption measurement.

The cesium sorption ratio was then calculated by

$$R_{dm} = \frac{A^o_{sm} - A_{tm} \cdot V}{A_{tm} \cdot V} \cdot \frac{V}{(1-f_d)W} ,$$

where

$$V = 15.0 + V_r .$$

The sorption ratios for all other species in the desorption measurement were then calculated using the sorption ratio for cesium and Eq.(3). An error analysis similar to that described earlier was also performed.

B. Results and Conclusions

The results for the R_d measurements for the ambient temperature conditions are given in Tables VIII and IX, while those obtained at the elevated temperatures are given in Table X. If no sorption ratio is listed in these tables for a given contact time, this is due to the difficulty of measuring the activity in the solution. This means that either the sorption ratio is too large or that

TABLE VIII

SORPTION RATIOS, SAMPLE CS5, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	R_d (mℓ/g)[a]				
			Cs	Sr	Ba	Ce(III)	Eu(III)
106-150	9.92		458 (2.8)	22.1 (4.2)	256 (4.4)	133 (4.6)	351 (4.3)
		55.72	756 (7.2)	27.7 (10.0)	391 (9.4)	5200 (13.2)	4550 (7.6)
	16.98		418 (2.7)	16.4 (4.0)	202 (4.3)	98.0 (4.5)	269 (4.2)
		27.66	620 (7.3)	22.4 (8.5)	252 (6.4)	1600 (7.5)	1870 (6.5)
	27.91		452 (2.8)	17.0 (4.8)	268 (4.4)	140 (4.6)	346 (4.3)
		13.67	576 (7.3)	23.1 (7.3)	257 (6.0)	753 (6.3)	1100 (6.0)
	62.04		516 (2.4)	18.9 (4.1)	415 (3.5)	1340 (3.9)	3580 (4.0)
250-355	9.91		220 (2.6)	12.7 (5.2)	75.3 (4.1)	102 (4.3)	193 (4.0)
		55.72	414 (7.3)	13.3 (8.5)	81.1 (5.5)	1050 (7.7)	1070 (5.6)
	16.98		252 (2.6)	12.0 (5.8)	95.9 (4.0)	90 (4.3)	205 (4.0)
		27.66	379 (7.4)	13.3 (7.7)	79.2 (5.2)	610 (5.8)	721 (5.2)
	27.91		282 (2.9)	10.8 (6.0)	79.7 (4.3)	86 (4.6)	185 (4.3)
		13.67	404 (7.3)	16.6 (9.5)	83.6 (6.7)	662 (7.1)	813 (6.7)
	62.03		283 (2.3)	13.0 (5.1)	150 (3.3)	366 (3.6)	1040 (3.4)
500-850	9.91		266 (2.6)	13.1 (5.4)	72.8 (4.0)	177 (4.2)	248 (3.9)
		55.72	660 (7.3)	17.2 (8.8)	77.4 (5.9)	1140 (8.4)	899 (5.9)
	16.97		306 (2.6)	12.3 (5.7)	78.3 (4.0)	116 (4.4)	222 (4.0)
		27.66	466 (7.3)	16.0 (9.2)	90.6 (6.3)	914 (7.0)	878 (6.3)
	29.97		303 (2.6)	12.3 (5.8)	77.2 (3.9)	118 (4.0)	214 (3.9)
		13.67	519 (7.3)	18.4 (8.4)	79.0 (6.4)	941 (6.8)	945 (6.3)
	62.03		411 (2.4)	11.1 (5.8)	77.7 (3.4)	186 (3.6)	367 (3.4)

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[a] The values in parentheses are the standard deviation of the R_d values expressed in percent.

TABLE IX

SORPTION RATIOS, SAMPLE CS7, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	R_d (mℓ/g)[a] Cs	Sr	Ba	Ce(III)	Eu(III)
106-150	9.90		351 (2.6)	23.1 (4.1)	230 (4.2)	77 (4.3)	211 (4.1)
		55.72	679 (7.2)	27.1 (7.2)	318 (5.5)	3150 (8.4)	3410 (5.6)
	16.99		402 (2.7)	23.0 (4.2)	286 (4.3)	177 (4.5)	464 (4.3)
		27.66	640 (7.3)	26.8 (7.5)	358 (5.9)	2180 (6.9)	2710 (6.0)
	27.96		550 (2.8)	24.0 (4.0)	380 (4.3)	349 (4.6)	782 (4.4)
		13.67	634 (7.3)	30.1 (7.8)	357 (6.4)	1360 (6.9)	1960 (6.4)
	62.02		719 (2.5)	26.4 (3.6)	473 (3.8)	681 (7.8)	1960 (8.1)
250-355	9.90		248 (2.6)	13.6 (5.2)	68.4 (4.0)	57 (4.3)	119 (4.0)
		55.72	614 (7.3)	13.7 (8.6)	74.8 (5.5)	1120 (8.6)	998 (5.6)
	16.98		341 (2.6)	15.5 (5.0)	83.9 (4.0)	86 (4.3)	171 (4.0)
		27.66	731 (7.3)	22.7 (8.4)	105 (6.1)	601 (7.3)	950 (6.1)
	27.96		342 (2.6)	14.1 (5.3)	106 (4.0)	112 (4.3)	235 (4.0)
		13.67	453 (7.3)	16.0 (8.1)	83.3 (6.0)	551 (6.4)	703 (6.0)
	62.02		533 (2.4)	14.3 (5.0)	96.8 (3.6)	253 (3.8)	602 (3.6)
500-850	9.89		464 (2.7)	16.9 (4.7)	90.8 (4.3)	168 (4.5)	284 (4.3)
		55.72	1030 (7.2)	20.5 (8.3)	96.7 (5.9)	1390 (7.7)	1170 (5.9)
	16.98		610 (2.9)	16.8 (4.7)	95.4 (4.5)	266 (4.7)	445 (4.4)
		27.66	1000 (7.3)	21.9 (7.2)	99.4 (5.7)	1120 (7.2)	1190 (5.7)
	27.96		480 (2.7)	15.5 (5.0)	93.3 (4.2)	131 (4.5)	258 (4.2)
		13.67	817 (7.2)	20.5 (7.6)	96.3 (6.0)	1050 (6.5)	1110 (6.0)
	62.02		775 (2.5)	15.4 (4.7)	95.6 (3.7)	421 (4.0)	845 (3.8)

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[a] The values in parentheses are the standard deviation of the R_d values expressed in percent.

TABLE X

SORPTION RATIOS, SAMPLE CS7, 70°C

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	R_d (mℓ/g)[a]				
			Cs	Sr	Ba	Ce(III)	Eu(III)
106-150	7.08		316 (2.6)	46.7 (3.0)	722 (4.4)	55 (4.3)	100 (4.1)
		55.75	991 (7.2)	58.9 (6.3)	1830 (5.7)	1310 (8.3)	1410 (5.7)
	17.05		442 (2.6)	62.1 (2.9)	1290 (4.6)	50 (4.3)	88 (3.8)
		27.72	796 (7.3)	61.9 (6.9)	1830 (6.2)	1390 (7.9)	1580 (6.3)
	27.93		673 (2.8)	56.9 (2.9)	1340 (4.8)	55 (4.7)	100 (4.3)
		13.69	1100 (7.2)	53.8 (6.7)	1180 (6.2)	665 (6.9)	807 (6.2)
	66.12		27800 (10.7)	151 (15.2)	2900 (15.3)	77 (15.2)	157 (15.2)
250-355	7.07		180 (2.4)	224 (4.0)	166 (3.7)	35 (4.1)	49 (3.8)
		55.75	1430 (7.2)	31.5 (7.1)	376 (5.6)	768 (10.0)	969 (5.7)
	17.04		226 (2.5)	28.8 (3.6)	320 (3.9)	25 (4.2)	39 (3.9)
		27.72	565 (7.3)	34.0 (7.7)	384 (6.3)	920 (8.8)	1200 (6.6)
	27.93		448 (2.7)	34.2 (3.3)	473 (4.3)	23 (4.5)	39 (4.1)
		13.69	775 (7.2)	32.5 (6.3)	465 (5.6)	949 (6.9)	1210 (5.9)
	66.11		14300 (7.4)	87.2 (10.6)	572 (10.5)	34 (10.5)	54 (10.5)
500-850	7.08		136 (2.5)	21.4 (4.0)	129 (3.9)	23 (4.3)	32 (4.0)
		55.75	4780 (7.4)	30.0 (7.1)	305 (6.1)	2310 (19.4)	1900 (6.4)
	17.04		189 (2.5)	25.2 (3.8)	183 (3.9)	22 (4.3)	32 (3.9)
		27.72	446 (7.4)	30.7 (7.5)	227 (5.9)	663 (8.0)	752 (6.1)
	27.92		209 (2.6)	24.7 (3.9)	190 (4.1)	28 (4.4)	45 (4.0)
		13.69	488 (7.3)	21.1 (6.6)	161 (5.6)	462 (6.6)	594 (5.8)
	66.11		4316 (4.1)	85.8 (6.2)	372 (5.9)	65 (6.1)	112 (5.9)

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[a] The values in parentheses are the standard deviations of the R_d values expressed in percent.

the decay time was too long (particularly important for ^{141}Ce). Limits for the R_d values have not been calculated.

The first batch (see Table V) of pre-equilibrated water was used for these measurements and the initial pH values were 7.69 and 7.74 for the ambient and elevated temperature materials, respectively. The final pH values are given in Tables XI and XII. These tables also include a parameter, L/S, which is simply the ratio of the R_d calculated using Eq.(1)(i.e., no correction for container effects) to the R_d calculated using Eq.(3)(i.e., corrected for container effects). Table XIII gives the final pH values for all control samples and also the percentage of the activity of each of the nuclides that remained in solution. The R_d values are shown graphically in Figs. 6-15. The observation that few of the L/S values are less than one indicates that the sampling of the solid phase was satisfactory for these measurements.

In examining Tables VIII-XII and Figs. 6-15 one can make several general observations. The scatter in the R_d values is sometimes larger than the quoted experimental uncertainties, assuming that one could expect a constant or monotonic behavior with time. This would indicate that strictly identical samples or conditions sometimes were not attained. There is an increase in the R_d values with time for all cations except strontium, where the value is very low and changes may be difficult to detect. This could be due to alteration of the minerals even at the rather low temperatures involved in these measurements. The significant increase in the cesium R_d value for a contact time of 8 weeks at 70°C also points to a change in the mineralogy.

At least qualitatively, an increase in the surface area (see Table IV) is accompanied by an increase in the sorption ratio. However, other factors, such as the mineral composition of the fractions,are undoubtedly significant.

The effect of increasing temperature varies with the element involved. The sorption ratios for cesium, strontium,and barium increase with temperature, while those for cerium and europium decrease. Presumably, the cerium and europium are more soluble at the higher temperature. One can expect that alteration or other geochemical processes would be accelerated at 70°C. Any change in the minerology of the solid might be expected to increase the sorption of the cesium, strontium,and barium since they usually are easily exchangable.

TABLE XI

pH AND L/S VALUES, AMBIENT TEMPERATURE

Core	Fraction (μm)	Sorption Time (days)	Final pH	Ce(III) L/S	Eu(III) L/S	Final Desorption pH
5	106-150	9.92	8.35	1.87	1.71	8.08
		16.98	8.10	1.76	1.61	8.20
		27.91	8.08	1.53	1.51	8.18
		62.04	8.26	1.38	1.34	
	250-355	9.91	8.38	1.24	1.23	8.10
		16.98	8.12	1.89	1.52	8.30
		27.91	8.08	1.56	1.36	8.32
		62.03	8.34	1.79	1.47	
	500-850	9.91	8.40	0.97	1.04	8.10
		16.97	8.16	1.77	1.49	8.34
		29.97	8.07	1.72	1.48	8.40
		62.03	8.25	2.03	1.65	
7	106-150	9.90	8.45	2.57	2.14	8.06
		16.99	8.19	1.71	1.49	8.47
		27.96	8.19	1.77	1.48	8.43
		62.02	8.35	1.97	1.76	
	250-355	9.90	8.34	1.69	1.38	8.13
		16.98	8.20	1.56	1.36	8.47
		27.96	8.10	1.77	1.41	8.47
		62.02	8.27	2.01	1.59	
	500-850	9.89	8.36	1.43	1.35	8.17
		16.98	8.18	1.13	1.13	8.48
		27.96	8.18	2.20	1.67	8.49
		62.02	8.22	1.97	1.67	

TABLE XII

pH AND L/S VALUES, CS7, 70°C

Fraction (μm)	Sorption Time (days)	Final pH	Ce(III) L/S	Eu(III) L/S	Desorption Final pH
106-150	7.08	8.05	1.00	1.11	8.23
	17.05	7.81	1.20	1.30	8.25
	27.93	7.78	1.37	1.40	8.50
	66.12	8.14	1.40	1.34	
250-355	7.07	8.28	1.54	1.69	8.21
	17.04	7.90	1.50	1.70	8.30
	27.93	7.58	1.54	1.62	8.48
	66.11	8.24	1.57	1.60	
500-850	7.08	8.21	1.17	1.42	8.15
	17.04	7.92	2.19	2.31	8.31
	27.92	7.80	1.72	1.72	8.46
	66.11	8.28	2.11	1.83	

TABLE XIII

PERCENT RECOVERY AND pH VALUES FOR CONTROL SAMPLES

Temperature (°C)	Contact Time (days)	Final pH	Percent Remaining in Solution				
			Cs	Sr	Ba	Ce(III)	Eu(III)
20	9.79	8.37	103	103	97.0	19.4	20.8
	16.97	8.10	103	102	95.3	16.6	17.4
	27.95	8.14	104	102	97.0	16.6	17.4
	62.01	8.26	105	104	96.7	12.5	12.8
70	7.06	8.26	103	102	102	66.0	52.6
	17.03	7.94	107	104	103	58.0	46.5
	27.92	7.81	108	105	102	51.6	40.6
	66.10	8.33	104	101	98.7	57.9	42.5

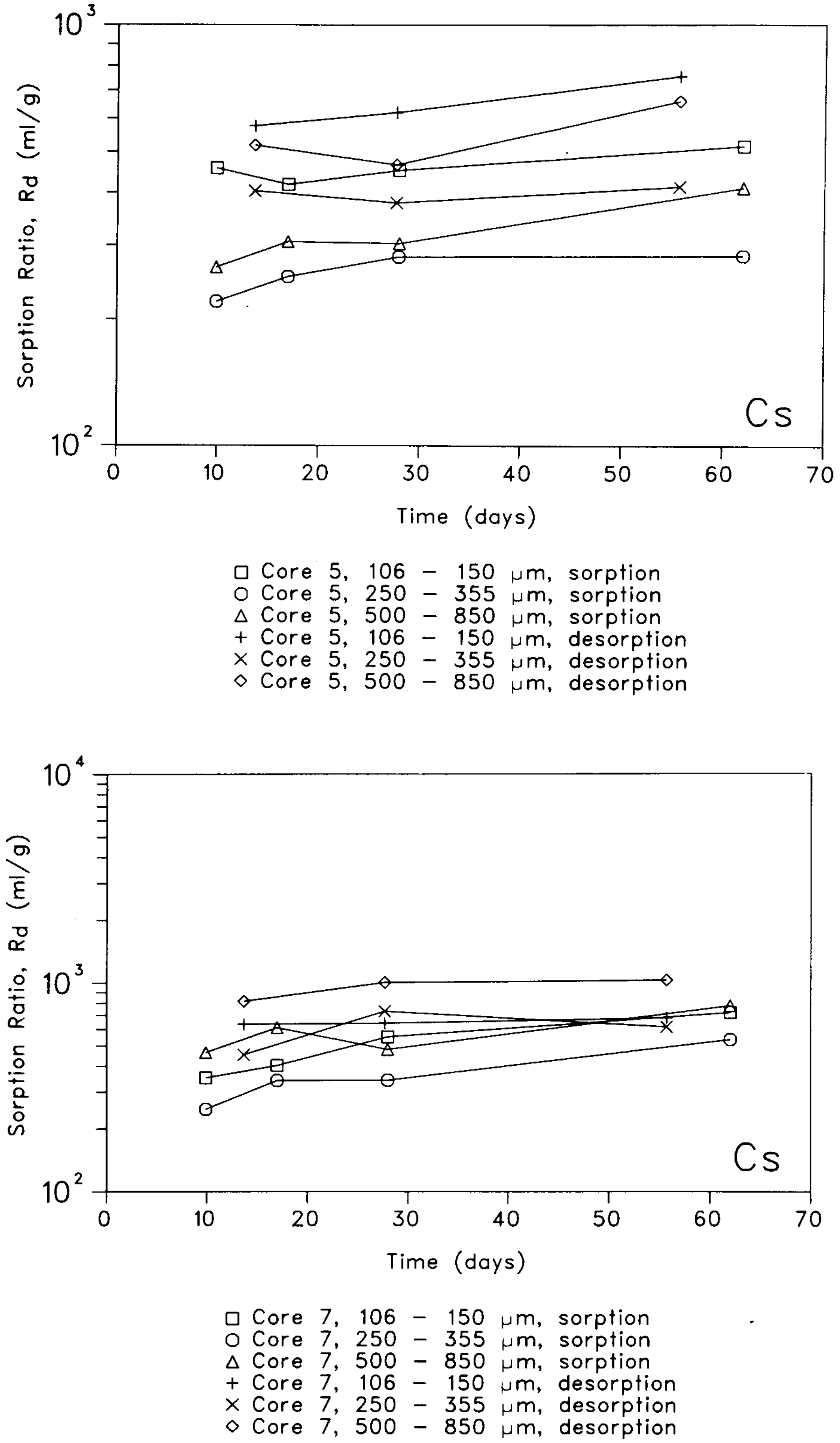


Fig. 6. Cesium sorption-desorption ratio measurements, ambient temperature.

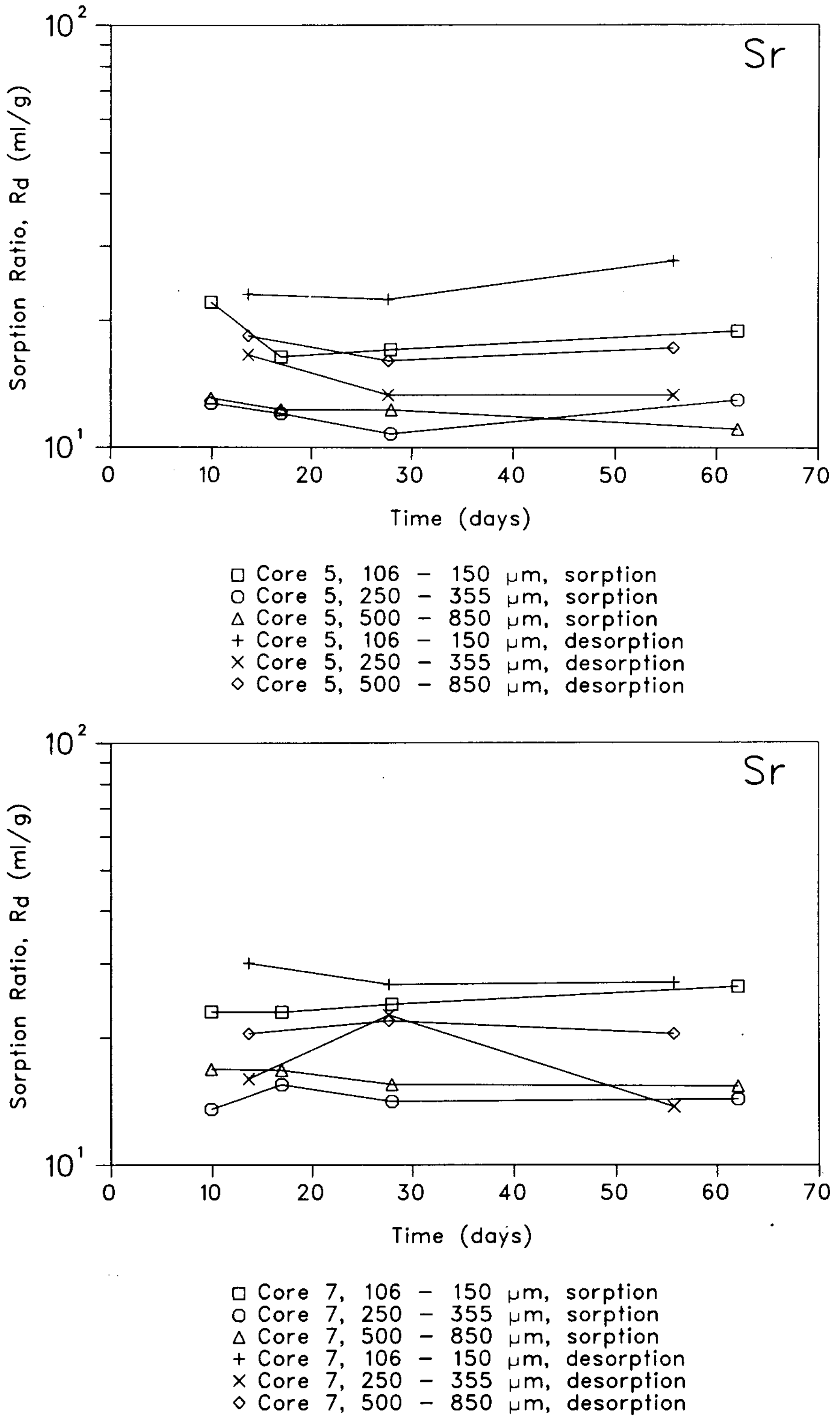


Fig. 7. Strontium sorption-desorption ratio measurements, ambient temperature.

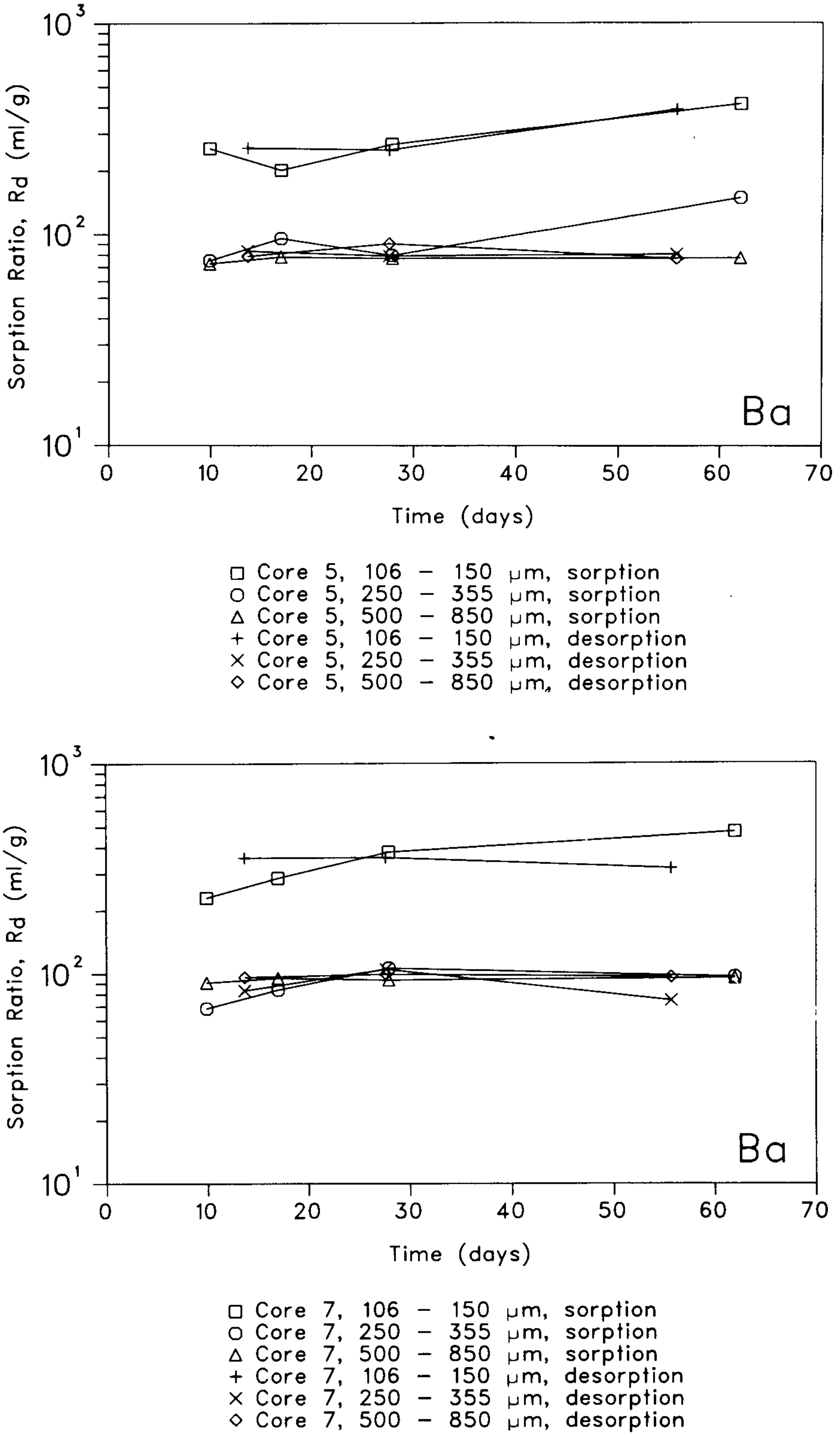


Fig. 8. Barium sorption-desorption ratio measurements, ambient temperature.

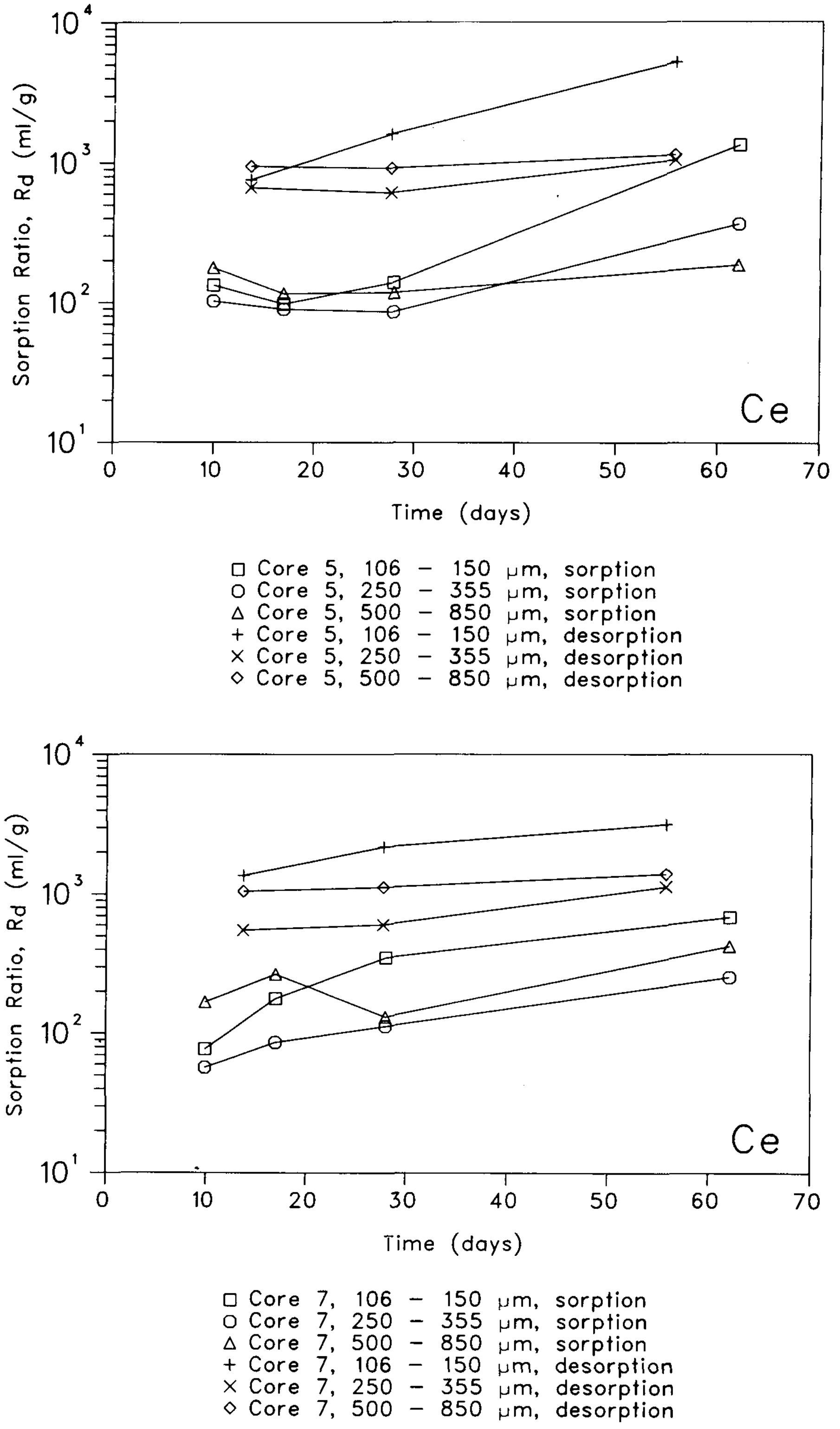


Fig. 9. Cerium sorption-desorption ratio measurements, ambient temperature.

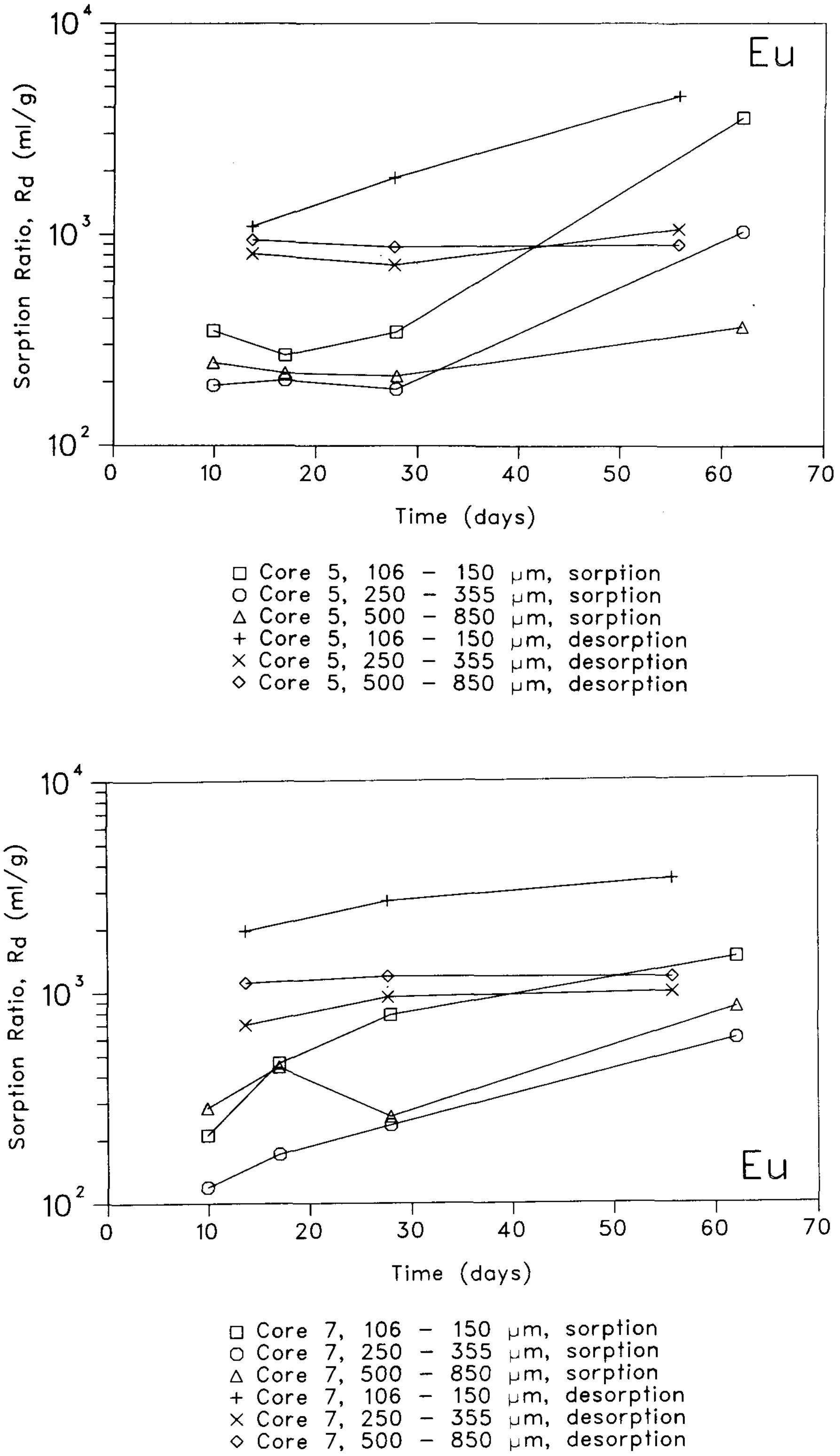


Fig. 10. Europium sorption-desorption ratio measurements, Ambient temperature.

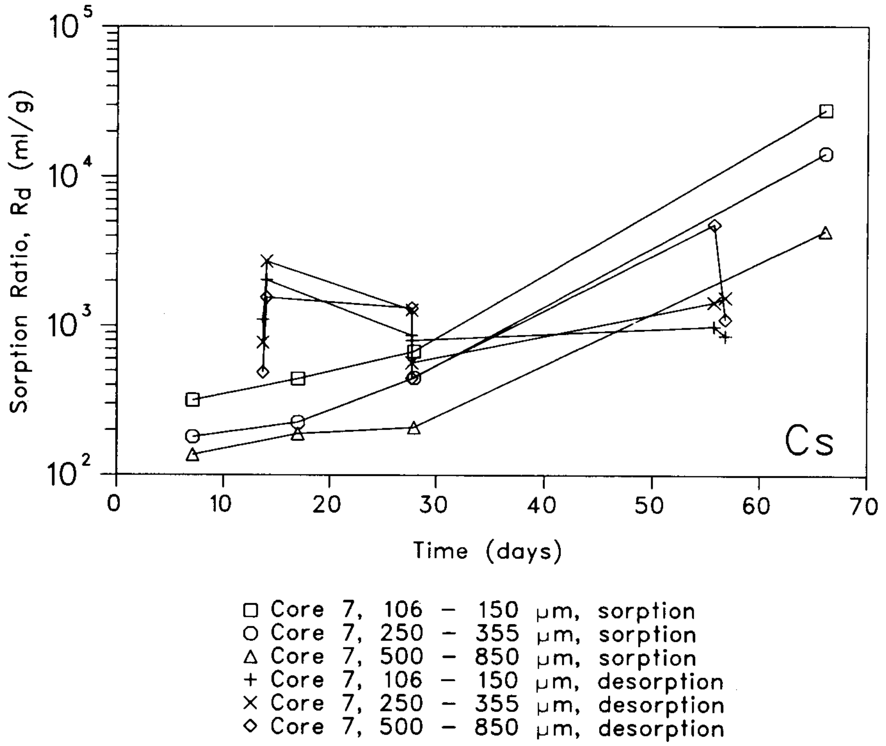


Fig. 11. Cesium sorption-desorption ratio measurements, 70°C.

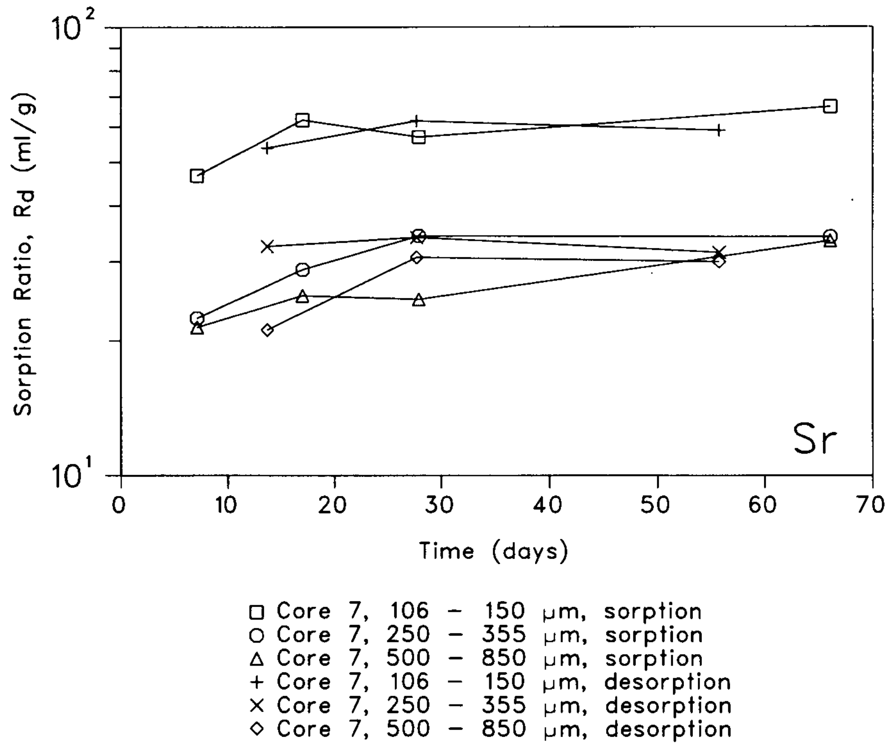


Fig. 12. Strontium sorption-desorption ratio measurements, 70°C.

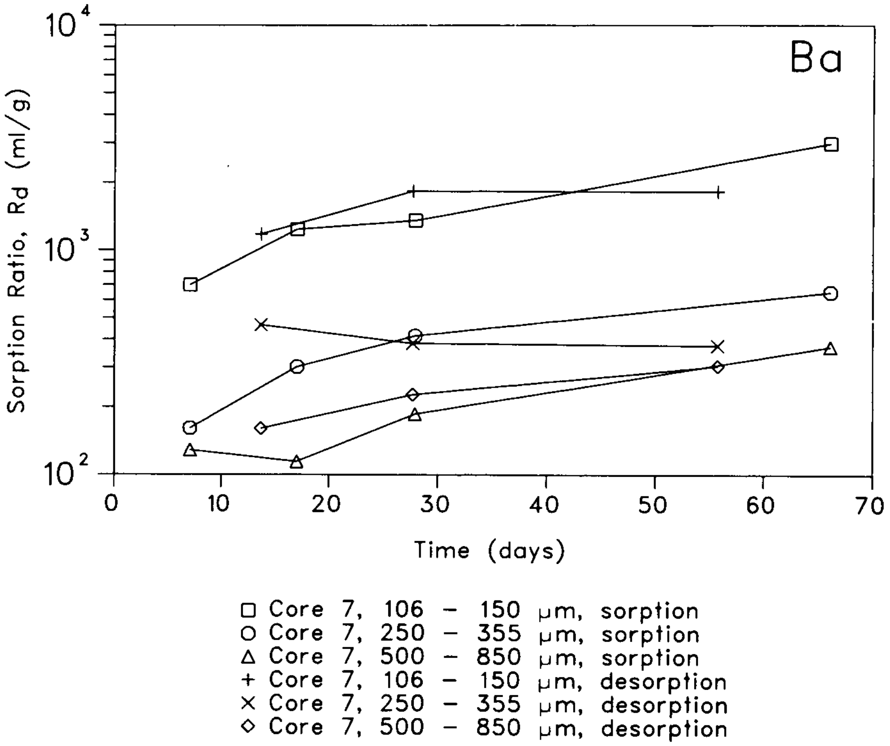


Fig. 13. Barium sorption-desorption ratio measurements, 70°C.

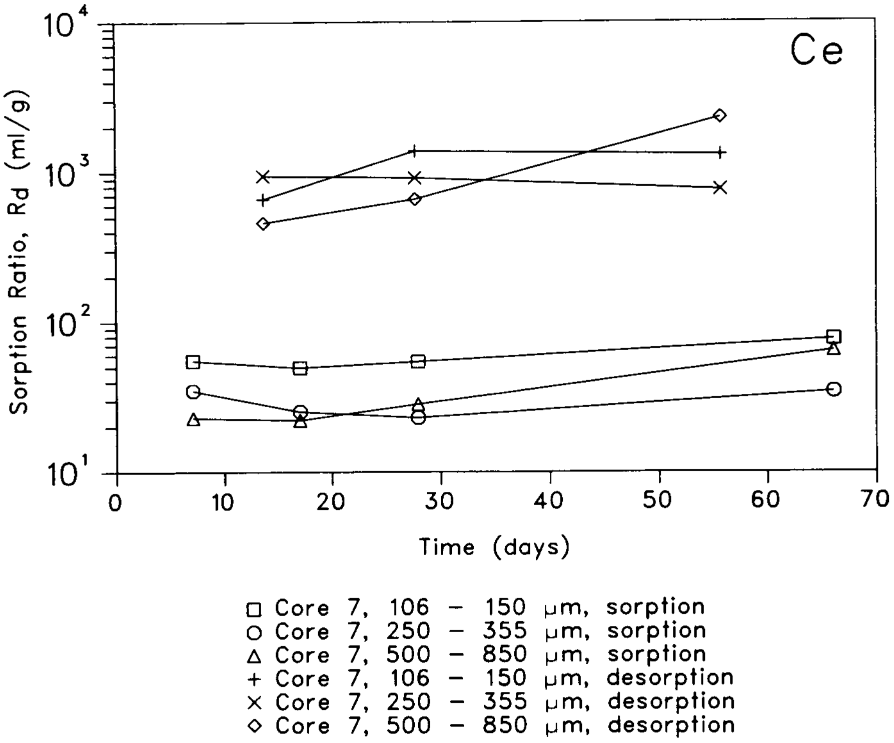


Fig. 14. Cerium sorption-desorption ratio measurements, 70°C.

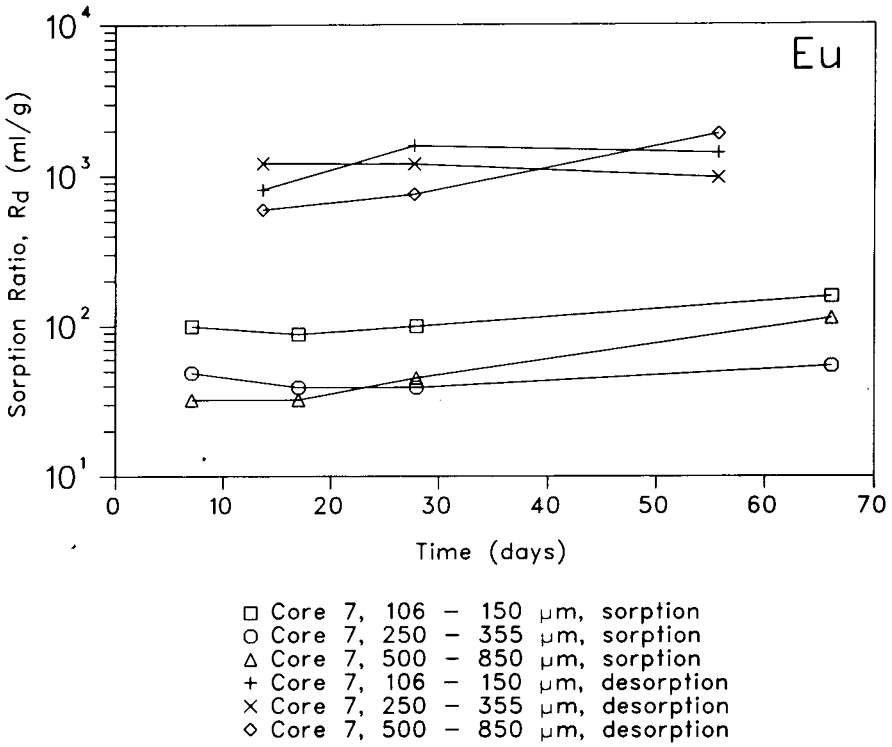


Fig. 15. Europium sorption-desorption ratio measurements, 70°C.

The R_d values reached by desorption are frequently (particularly Ce and Eu) significantly greater than those reached by sorption. One can speculate that this observation may be a consequence of the following phenomena. The solution from which sorption takes place may contain different species of the same element (for example, ions of different oxidation states, differently complexed ions, and various degrees of hydration or polymerization). If the exchange between such species is very slow and they exhibit different sorption characteristics, only one species may sorb strongly while the other remains in solution. The nonsorbing species is then absent in the desorption experiment. Of course, one could also explain this observation by postulating a significant alteration of the mineralogy in such a manner as to greatly increase the clay and zeolite fractions on the surface of the solid phase. Since clays and zeolites have a strong affinity for cations, one would then expect a higher sorption ratio. There is also the possiblity of diffusion into the solid itself.

The pH does not seem to have a major effect on the sorption ratio values for cesium, strontium,and barium. It should have an effect on cerium and europium since these elements tend to form insoluble hydroxides at pH 8 to 8.5. This is probably the effect indicated in Table XIII. However, temperature and complexing may also be rather important.

The need to sample the solid phase in order to measure the sorption ratio for those species having container problems is very clear (see Table XI and XII). Of course, the addition of the solid should reduce the percentage of the activity going to the wall due to the greater surface area of the solid. However, for granites the magnitude of the effect of the container is significant, as indicated by the L/S ratio in Tables XI and XII.

Table XIV gives the mean sorption ratio values for all samples for each of the core samples at the two different temperatures. Even though there are some particle size effects on the R_d values, the ranges are only a factor of 2 to 3. The increasing sorption with time is also sufficiently low that using a simple average is reasonably justified. These average values indicate that the elements arranged in the order of increasing sorption ratio at ambient temperature is: Sr, Ba, Ce(III), Cs, and Eu(III), while at 70°C the order is: Sr, Ce(III), Eu(III), Cs, and Ba. At elevated temperature, the sorption ratios, for Sr, Ce(III), and Eu(III) are all below 100 mℓ/g. The quoted uncertainties in Table XIV are the standard deviations of the population.

IV. SORPTION OF TECHNETIUM

A. Measurement Technique

Measurements of the sorption behavior of technetium, under atmospheric oxygen conditions, have been made following exactly the same procedures as described earlier in this report (see Section III.A.). The measurements were made using the ^{95m}Tc supplied through Battelle (PNWL). The second batch (see Table V) of pre-equilibrated water was used. The initial pH values were 7.62 and 8.09 for the ambient and 70°C experiments, respectively. Since the container sorption problems for technetium were unknown, ^{137}Cs was also added to the water (17 μCi ^{137}Cs/ℓ final solution) using the evaporation procedure previously described. However, the ^{95m}Tc was added by simply pipetting a fraction of the diluted tracer into the appropriate water prior to filtration. The pH did not require adjusting after this addition. The final concentration was 4.1 μCi ^{95m}Tc/ℓ solution. Only the solid fractions from CS7 were used for these measurements. The same two temperatures, 22 ± 2°C and 70 ± 1°C, were also used.

TABLE XIV
MEAN SORPTION RATIOS

Element	Core	Temp. (°C)	Sorption Ratio, R_d (mℓ/g) Sorption	Sorption Ratio, R_d (mℓ/g) Desorption
Cs	CN5	20	347±28	533±43
	CN7	20	328±48	734±63
	CN7	70 [a]	313±59	1260±452
Sr	CN5	20	14.3±1.0	18.7±1.6
	CN7	20	18.2±1.3	22.1±1.8
	CN7	70	38.0±4.6	39.4±4.9
Ba	CN5	20	154±32	155±39
	CN7	20	175±39	176±42
	CN7	70	718±239	751±266
Ce	CN5	20	246±102	1430±482
	CN7	20	232±52	1390±272
	CN7	70	41.1±5.4	1050±187
Eu	CN5	20	602±279	1430±410
	CN7	20	489±111	1580±308
	CN7	70	70.6±11.5	1160±141

---

[a] The 8-wk sorption contact time samples were not used.

B. Results and Conclusions

The results for the R_d measurements for the ambient and elevated temperature conditions are given in Tables XV and XVI, respectively, and in Figs. 16-19. The sorption ratios for technetium were calculated using Eq. 1 since no container sorption was found for ^{95m}Tc (see Table XVII). The R_d values are shown graphically in Figs. 16-19.

The effect of particle size and temperature on the technetium sorption is not completely clear. The particle size (surface area) does not play as large a role for technetium as for the other species studied. There may even be an inverse relationship with particle size at 22°C. There does not seem to be a

TABLE XV

Cs AND Tc(VII) SORPTION RATIOS, SAMPLE CS7, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	Final pH	R_d (mℓ/g)[a]	
				Cs	Tc(VII)
106-150	6.49		8.06	141 (1.2)	31.6 (3.4)
		56.78	7.72	581 (11)	196 (21)
	13.53		8.02	161 (1.2)	43.6 (3.3)
		27.70	8.68	451 (11)	214 (20)
	27.60		8.00	172 (1.7)	160 (2.9)
		14.01	7.83	392 (11)	599 (30)
	55.58		8.02	188 (1.6)	80.5 (2.5)
250-355	6.58		8.17	83 (1.1)	-0.7 (51)
		56.78	7.84	338 (10)	- 30 (12)
	13.52		8.06	103 (0.8)	-0.3 (114)
		27.70	8.62	340 (10)	- 42 (16)
	27.59		7.67	111 (1.8)	-0.9 (38)
		14.01	7.86	292 (11)	- 23 (9.1)
	55.58		8.06	128 (1.7)	-0.9 (36)
500-850	6.58		8.24	76.8 (1.1)	-0.8 (42)
		56.77	7.87	342 (10)	- 37 (15)
	13.52		8.02	101 (1.1)	-0.9 (38)
		27.70	8.59	368 (11)	- 34 (13)
	27.59		7.82	121 (1.8)	-0.7 (49)
		14.01	7.87	319 (10)	- 33 (14)
	55.57		8.12	125 (1.6)	-1.1 (29)

---

[a] The values in parentheses are the standard deviation of the R_d values expressed in percent.

TABLE XVI

Cs AND Tc(VII) SORPTION RATIOS, SAMPLE CS7, 70°C

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	Final pH	R_d (mℓ/g)[a]	
				Cs	Tc(VII)
106-150	6.83		7.56	221 (1.3)	22.7 (4.0)
		56.76	8.48	858 (11)	101 (19)
	13.84		7.93	495 (1.7)	60.7 (3.1)
		27.71	8.64	862 (11)	242 (21)
	27.84		7.96	1580 (2.2)	27.2 (3.5)
		14.04	8.32	2030 (14)	419 (30)
	55.83		7.96	3560 (2.0)	1.3 (29)
250-355	6.83		7.94	144 (1.7)	0.7 (60)
		56.76	8.37	1550 (13)	- 0.8 (415)
	13.83		7.97	332 (1.4)	0.4 (97)
		27.70	8.59	1270 (13)	-8.0 (17)
	27.84		7.97	1370 (2.4)	0.3 (108)
		14.04	8.26	2700 (15)	-8.9 (6.7)
	55.82		7.68	2460 (1.9)	-1.3 (24)
500-850	6.82		8.00	104 (1.1)	3.1 (15)
		56.76	8.45	1100 (7.2)	104 (41)
	13.83		8.14	302 (1.4)	-0.3 (107)
		27.70	8.55	1310 (13)	- 24 (9.9)
	27.84		8.12	477 (1.9)	-0.2 (190)
		14.04	8.57	1550 (13)	- 19 (6.7)
	55.81		7.78	2820 (1.9)	24.6 (3.3)

---

[a] The values in parentheses are the standard deviations of the R_d values expressed in percent.

TABLE XVII

PERCENT RECOVERY AND pH VALUES FOR THE CONTROL SAMPLES

Temperature (°C)	Contact Time (days)	Final pH	Percent Remaining in Solution	
			Cs	Tc(VII)
20	6.57	8.27	99.4	102
	13.54	8.08	101	105
	27.40	7.93	102	104
	55.57	8.18	88.6	105
70	6.81	8.10	98.9	101
	13.82	8.07	101	103
	27.82	8.15	99.8	101
	55.83	7.96	77.9	104

consistent temperature effect since the sorption increased for some samples and decreased for others when the temperature was increased.

The presence of iron in the mineral fractions cannot be excluded, particularly since the pulverizing was done in an iron system. FeO has also been observed in this geologic material.[22] Since reducing conditions lead to significant loss of Tc from solution 23, this may cause the high R_d values in the fine sieve fractions.

In addition, one should note that the cesium sorption ratios observed are rather different than those reported earlier (see Tables IX and X) for the same materials. This difference is a factor of about 3. This may be the result of a different batch of water being used or by changes in the rock itself since the sieved fractions had been stored for several months between the different measurements. There also seems to be a much faster increase in the sorption ratio with time at 70°C than observed before.

The mean sorption ratios for technetium for all measurements are 25.8 ± 49.6 mℓ/g and 11.6 ± 18.8 mℓ/g for the ambient and 70°C conditions, respectively. Similarly, the mean sorption ratios for cesium are 126 ± 34 mℓ/g and 1160 ± 1200 mℓ/g for the two temperature conditions.

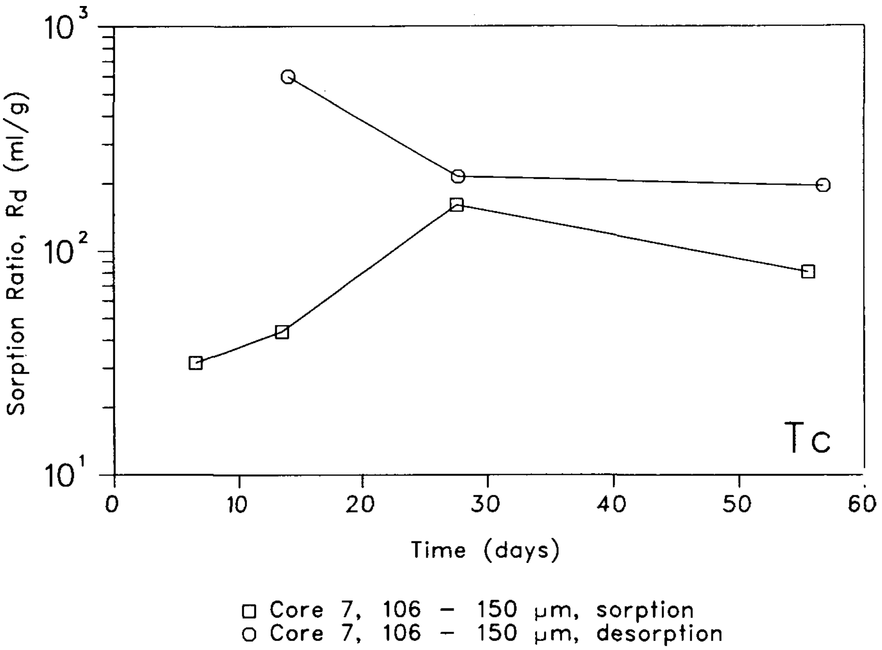


Fig. 16. Technetium(VII) sorption-desorption ratio measurements, ambient temperature.

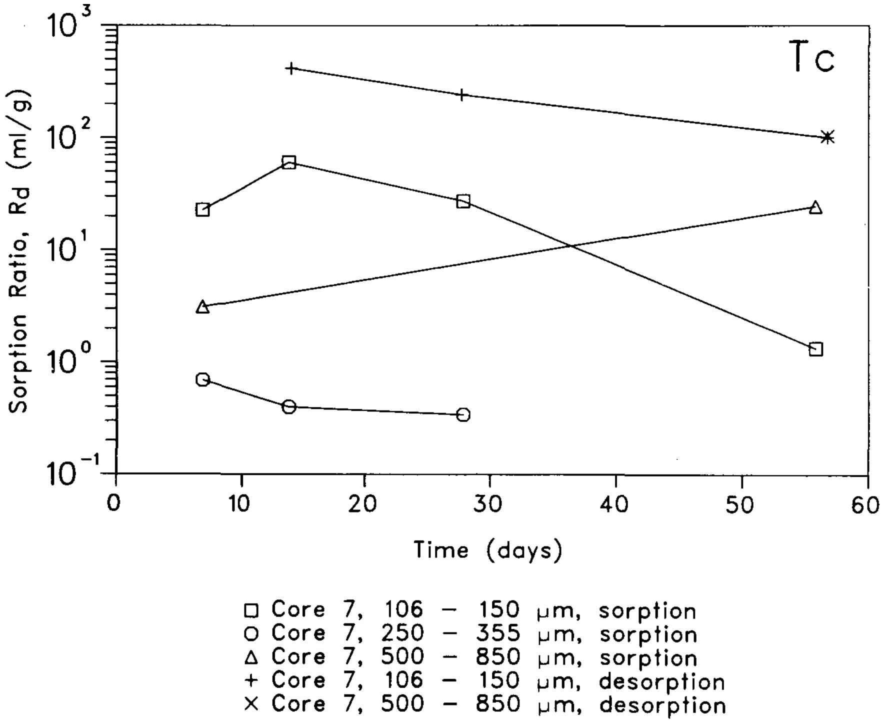


Fig. 17. Technetium(VII) sorption-desorption ratio measurements, 70°C.

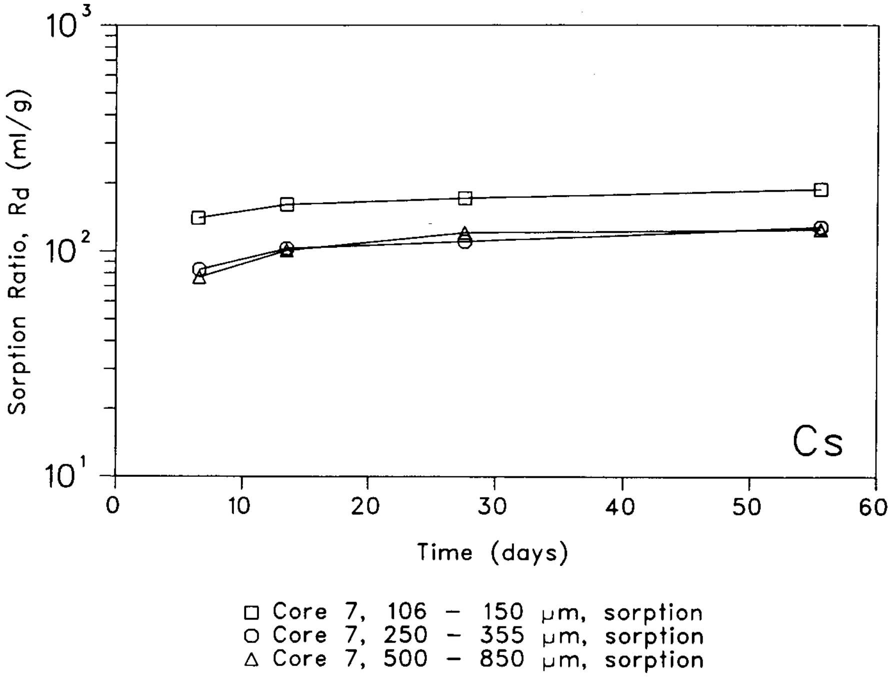


Fig. 18. Cesium sorption-desorption ratio measurements, ambient temperature.

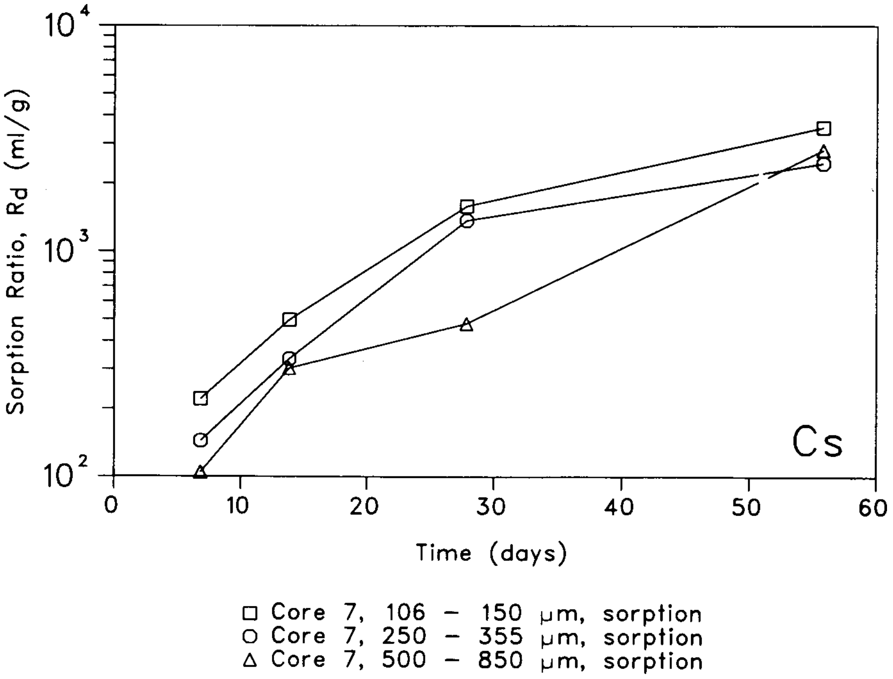


Fig. 19. Cesium sorption-desorption ratio measurements, 70°C.

V. SORPTION OF URANIUM(VI)

A. Measurement Technique

Measurements of the sorption behavior of uranium have been made using procedures similar to those reported earlier (see Section III.A.). The ^{237}U used in these measurements[24] was made by the $^{236}U(n,\gamma)^{237}U$ reaction in the HFIR at the Oak Ridge National Laboratory. The purification chemistry was done at Oak Ridge. It consisted of a dissolution in $HCl-HNO_3$, a conversion to the nitrate, an extraction with ethyl acetate, an anion column washed with 5M HCl-0.1M HF, and an elution with water. The ^{237}U thus prepared was used, after dilution, with batch 3 of the pre-equilibrated waters (see Table V). The tracer had a specific activity of 1 Ci/mg and the final concentration in the tagged water was $\sim 5.4 \times 10^{-8}$ M. Measurements were made only at ambient temperature.

The assay of the radioactivity was done using a 3 in. x 3 in. external NaI(Tl) detector and multichannel analyzer. The solutions were prepared for counting as previously described. The activity of the ^{237}U was obtained by integrating the energy region between 35 and 360 keV. The standard deviation of the assay was assumed to be 5%.

Since the control samples indicated that there was no sorption of uranium on the container, Eq. 1 was used to calculate the sorption ratio. Since these measurements were somewhat exploratory, the initial and final pH values, and the amount of wash solution (g_r) left with the solid sample, were not measured, but g_r was assumed to be 0.5 g. Due to the short half-life of ^{237}U, the sorption contact times were 1, 2,and 3 weeks, and the desorption contact times were 3, 2, and 1 week, respectively.

B. Results and Conclusions

The results of the measurement of the uranium(VI) sorption ratios are given in Tables XVIII and XIX, and are shown graphically in Fig. 20. Their fraction of the ^{237}U in the control samples for the 1, 2,and 3 week contact times were 101%, 97.9%,and 99.4%, respectively. The uranium(VI) is poorly sorbed on these granite samples, and there is an increase in the sorption ratio with increasing surface area. There is good agreement between the R_d values for the two different core materials (CS5 and CS7) used.

Presumably the low sorption of uranium(VI) is due to the rather high carbonate concentration in these waters that would complex the uranyl ion strongly.

TABLE XVIII

U(VI) SORPTION RATIOS SAMPLE CS5, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	R_d (mℓ/g)[a] U(VI)
106-150	6.95		9.9 (22)
		19.76	26.6 (53)
	13.95		10.1 (22)
		13.64	14.6 (71)
	20.95		10.4 (21)
		7.89	3.8 (186)
250-355	6.95		2.2 (72)
		19.76	24.7 (55)
	13.95		2.0 (80)
		13.64	8.0 (106)
			3.1 (52)
		7.89	-12.4 (18)
500-800	6.95		3.3 (50)
		19.76	26.6 (53)
	13.95		0.4 (360)
		13.64	14.6 (71)
	20.95		1.3 (117)
		7.89	3.9 (186)

---

[a] The values in parentheses are the standard deviations of the R_d values expressed in percent.

TABLE XIX

U(VI) SORPTION RATIOS SAMPLE CS7, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	R_d (mℓ/g)[a] U(VI)
106-150	6.95		10.7 (21)
		19.76	21.6 (58)
	13.95		8.2 (24)
		13.64	6.0 (130)
	20.95		8.8 (23)
		7.89	-1.4 (400)
250-355	6.95		2.3 (70)
		19.76	19.5 (60)
	13.95		2.8 (55)
		13.64	17.1 (64)
	20.95		1.9 (80)
		7.89	1.1 (610)
500-800	6.95		0.6 (260)
		19.76	21.6 (58)
	13.95		1.0 (147)
		13.64	6.0 (128)
	20.95		1.1 (143)
		7.89	-1.4 (400)

---

[a] The values in parentheses are the standard deviations of the R_d values expressed in percent.

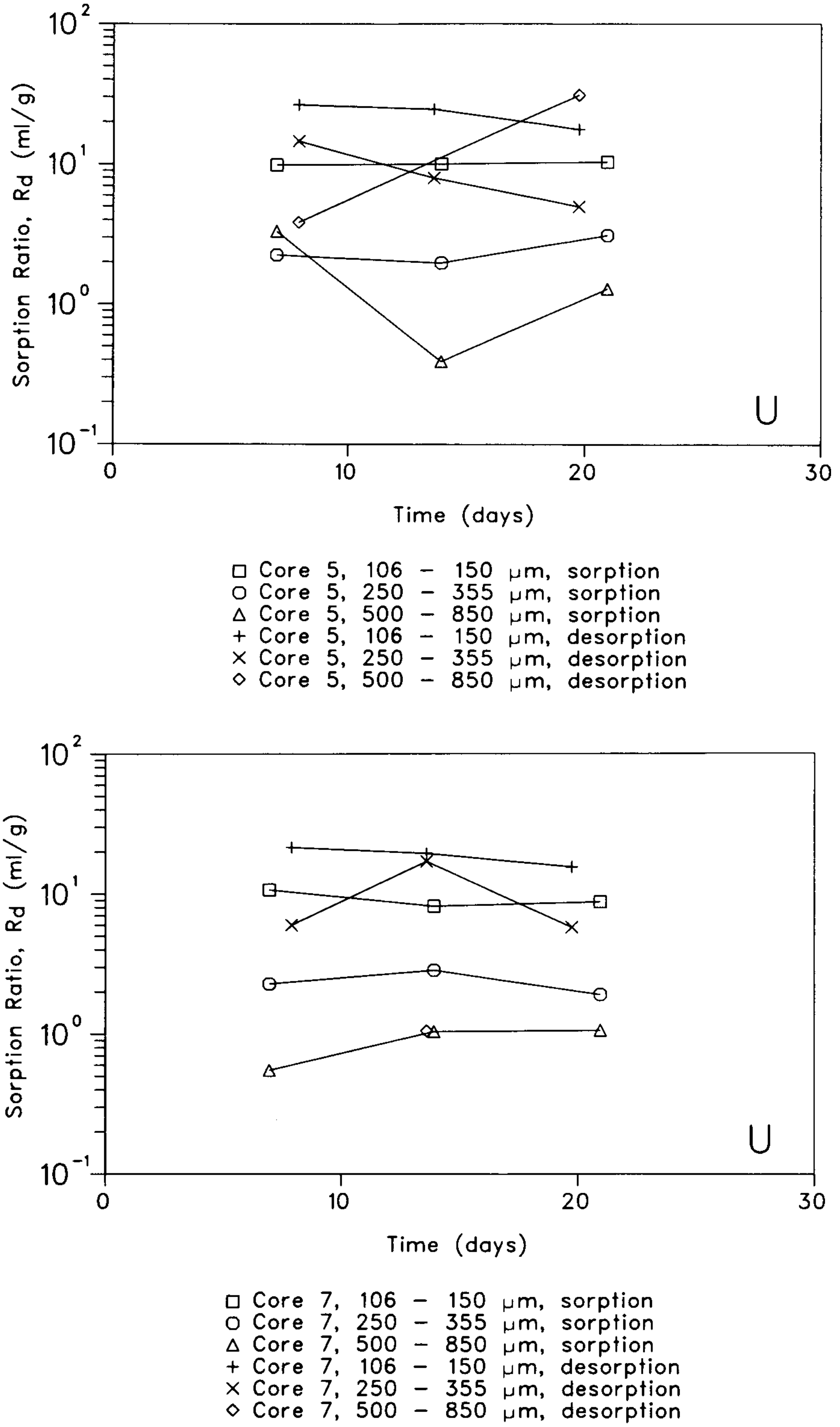


Fig. 20. Uranium (VI) sorption-desorption ratio measurements, ambient temperature.

The mean sorption ratios for uranium(VI) for all measurements are 4.4 ± 1.2 mℓ/g and 4.2 ± 1.3 mℓ/g for the CN5 and CN7 samples, respectively. Similarly, the desorption values are 16.5 ± 3.8 mℓ/g and 12.4 ± 3.0 mℓ/g.

VI. SORPTION OF PLUTONIUM AND AMERICIUM

A. Measurement Techniques

1. Preparation of Tagged Solutions

The traced waters used in these studies were prepared using the pre-equilibrated waters described Section III.G, and ^{237}Pu tracer obtained from the Argonne National Laboratory, and isotopically pure ^{241}Am tracer obtained from Oak Ridge National Laboratory. Tracer purities were checked by both alpha and gamma spectroscopy. The specific activities of the tracers were measured by alpha and gamma counting: ^{237}Pu $\approx 2.5 \times 10^6$ dpm/mℓ at feed preparation time, ^{241}Am $= 7.23 \times 10^8$ dpm/mℓ. Feed solutions were prepared so as to contain $\approx 3.3 \times 10^3$ dpm/mℓ of ^{237}Pu and $\approx 2 \times 10^6$ dpm/mℓ of ^{241}Am at 100% yield of tracer in water, which was generally not the case (see below). These correspond to mass concentrations of $\approx 10^{-12}$ M Pu and $\approx 10^{-6}$ M Am. Stock tracer solutions were in 3 M HCl and an attempt was made to hold the added chloride concentration constant at ≈ 0.014 M by adding 3 M HCl when the volume of tracer used was reduced. The ^{237}Pu tracer was treated with $NaNO_2$ so that the Pu was in the IV oxidation state at the beginning. This step resulted in the addition of $\approx 10^{-4}$ M sodium ion to the feed solution containing plutonium. Tracer solutions were evaporated to dryness in open polypropylene tubes at room temperature; this required several days when volumes were large. Twenty milliliters of the appropriate pre-equilibrated ground water was then added to each tube. The tubes were capped and shaken vigorously for three minutes. The tubes were centrifuged for one hour at 12 000 rpm and then the contents were transferred to clean polyethylene bottles. This process was repeated three times: the first two for brief shaking periods and the third with overnight shaking in a mechanical shaker. Additional water was added to the bottles containing the incomplete traced feed solutions, and these were also shaken overnight. The next day the tubes were once again centrifuged and the solutions added to the bulk solutions. All "empty" tubes were checked after each step for gamma activity.

The feed solutions were made up to final volumes, shaken for at least an hour, and centrifuged for one hour. Aliquots were then taken and acidified for later assay of the initial activities of each tracer in the solutions, although this information was not used in later calculations of the sorption ratios (see below). An aliquot of each solution was taken for measurement of pH. Within one hour, aliquots of the solutions were added to ground rock samples and sorption measurements were started. The feed solutions were not filtered because earlier experiments suggested that major fractions of the Am and Pu activities remain on the filters. The yields of tracer in the feed solutions ranged from 15 to $>$ 50% for water pre-equilibrated at room temperature, but were $<$ 5% for two solutions prepared with water pretreated at 70°C.

2. Sorption Measurements

Crushed rock from cores CS5 and CS7 was again used for sorption studies at both ambient (22 ± 2°C) and elevated (70 ± 1°C) temperatures. The material was pretreatedd by shaking weighed one-gram quantities with 20-mℓ portions of the appropriate pre-equilibrated synthetic ground water for periods of at least two weeks. The samples were contained in prewashed, capped 40-mℓ polypropylene tubes. The phases were then separated by centrifuging at 12 000 rpm for one hour. The weight of the wash solution remaining with the solid phase was obtained by weighing the tube and solid before and after the pre-equilibration.

Twenty-mℓ portions of traced feed solution of known pH were added to the tubes containing crushed rock. The solids were dispersed by vigorous shaking and the mixtures were agitated gently for selected times: 1, 2, 4,and 8 weeks. The shaking rates were 200 oscillations per minute for the ambient temperature samples, and 80 oscillations per minute for the 70°C samples.

At the end of a shaking period, the aqueous phases were separated from the solids by four centrifugings, each in a new tube, for one hour at 12 000 rpm. Aliquots of the final solutions were taken for pH measurements, gross gamma counting and gamma spectroscopy. The solid phases were left in the tubes and counted directly. Since this procedure meant that any activity sorbed on the walls of the container was also counted, several solid samples were carefully removed from the tubes and the tubes were checked for residual activity. In general, less than 10% of the activity remained; appropriate corrections were included in the calculations.

The comments concerning "control" samples with traced aqueous phases but no solid in Section III.A.2 are applicable here. Such samples run with Pu and Am indicated that about 50% of the activity sorbed on the tubes when no solid was present.

3. Assay of Radioactivity

Both liquid and solid samples were counted on a calibrated 23%, coaxial Ge(Li) detector. The 1024-channel spectra were recorded in a multichannel analyzer which is connected to the PDP-9 computer described earlier. A minimum of two counts were taken for each sample. Data were analyzed primarily by hand. The 60-keV photopeak was integrated and the Compton contribution due to the ^{227}Pu was subtracted to obtain the ^{241}Am activity, while the total x-ray region was integrated for ^{237}Pu. Each region was corrected for a minor contribution from the other nuclide. Counting standards were prepared using known amounts of ^{241}Am and of ^{237}Pu in the same geometries and conditions as the experimental samples. These were used to correct for the different efficiencies of liquid and solid samples.

Samples containing only ^{241}Am were also counted on a NaI(Tl) detector in an analogous manner in order to verify the Ge(Li) results.

4. Calculations

Since both solid and liquid phases were counted directly for ^{237}Pu and ^{241}Am, the distribution ratio (see Section III.A.5) can be calculated directly as:

$$R_d = \frac{\text{activity in solid phase per unit mass of solid}}{\text{activity in solution per unit volume of solution}} .$$

The activities in the control samples were not used in the calculations. A small correction was applied for the container effect.

B. Results and Conclusions

The results for the distribution ratio measurements for ambient temperature conditions are given in Tables XX and XXI while those obtained at elevated temperature are given in Tables XXII and XXIII. The third batch (see Table V) of pre-equilibrated water was used for the ambient temperature studies while the second batch of the elevated temperature water was used for the measurements at 70°C. The initial and final pH values are given in Tables XXIV-XXVII. The R_d values are shown graphically in Figs. 21-24. Mean sorption values for four and eight week contact times are given in Table XXVIII; all available desorption data were averaged.

TABLE XX

Pu AND Am SORPTION RATIOS, SAMPLE CS5, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	R_d (mℓ/g)* Pu	R_d (mℓ/g)* Am
106-150	7.7			1200
		19.7		470
	14.7			3200
	14.7		1400	2900
		15.7		2900
	28.7		1200	5300
	56.7		2300	6800
		16.8		750
	56.7			8700
		16.8		790
250-355	7.7			760
		29.7		330
	14.7		980	1300
		19.7		320
	28.7		710	1700
	56.7		2500	3000
		16.8		445
500-850	7.7			360
		19.7		380
	14.7		400	480
		19.7		420
	28.7			2600
	28.7		520	680
		15.7		3000
	56.7		840	4100

TABLE XXI

Pu AND Am SORPTION RATIOS, SAMPLE CS7, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	R_d (mℓ/g)*	
			Pu	Am
106-150	7.7			2200
	14.7		1100	2300
		15.7		18000
	28.7		1500	8500
	56.7		2900	3700
	56.7			3100
	56.7			4800
		16.8		540
250-355	7.7			780
		15.7		1000
	14.7		510	1100
		15.7		3700
	28.7		600	1700
		19.7		620
	56.7		970	2400
		16.8		220
500-850	7.7			540
	7.7			530
		29.7		240
	14.7		690	870
		19.7		150
	14.7			1200
		29.7		440
	28.7		1200	2000
	28.7			1400
	28.7			1700
	56.7		2500	4200
	56.7			5200
	56.7			1700
		16.8		500

TABLE XXII

Pu AND Am SORPTION RATIOS, SAMPLE CS5, 70°C

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	R_d (mℓ/g)*	
			Pu	Am
106-150	7.7			6200
		19.7		375
	14.7		3500	4500
	28.7		4300	17 000
	56.7		9400	18 000
		16.8		460
500-850	7.7			1000
	14.7		280	1800
	28.7		500	2400
		15.7		1900
	56.7		700	2000

TABLE XXIII

Pu AND Am SORPTION RATIOS, SAMPLE CS7, 70°C

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	R_d (mℓ/g(*	
			Pu	Am
106-150	7.7			2300
	14.7		3600	4400
	28.7		4400	11 000
	56.7		25 000	63 000
		16.8		400

TABLE XXIV

pH VALUES, SAMPLE CS5, AMBIENT TEMPERATURE

Fraction (µm)	Sorption Time (days)	Desorption Time (days)	Initial pH	Final pH
106-150	7.7		8.00	8.23
		19.7	7.96	8.21
	14.7		8.00	7.46
	14.7		8.09	6.32
	15.7		7.96	8.26
	28.7		8.09	8.03
	56.7		8.09	8.25
		16.8	8.13	7.97
	56.7		8.00	8.36
		16.8	8.13	8.30
250-355	7.7		8.00	8.16
		29.7	8.04	8.35
	14.7		8.09	7.74
		19.7	7.96	8.20
	28.7		8.09	8.18
	56.7		8.09	8.20
		16.8	8.13	8.12
500-850	7.7		8.00	8.22
		19.7	8.04	8.35
	14.7		8.09	7.60
		19.7	7.96	8.33
	28.7		8.00	8.30
	28.7		8.09	8.08
		15.7	7.96	8.32
	56.7		8.09	8.32

TABLE XXV

pH VALUES, SAMPLE CS7, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	Initial pH	Final pH
106-150	7.7		8.00	7.90
	14.7		8.09	7.73
		15.7	7.96	8.27
	28.7		8.09	8.26
	56.7		8.09	8.38
	56.7		8.00	8.41
	56.7		8.00	8.37
		16.8	8.13	8.30
250-355	7.7		8.00	7.94
		15.7	8.04	8.15
	14.7		8.09	8.08
		15.7	7.96	8.13
	28.7		8.09	8.22
		19.7	7.96	8.34
	56.7		8.09	8.37
		16.8	8.13	8.05
500-850	7.7		8.09	7.98
	7.7		8.00	8.21
		29.7	8.04	8.42
	14.7		8.09	8.04
		19.7	7.96	8.30
	14.7		8.00	7.72
		29.7	8.04	8.39
	28.7		8.09	8.29
	28.7		8.10	8.21
	28.7		8.12	8.01
	56.7		8.09	8.42
	56.7		8.10	8.40
	56.7		8.12	8.29
		16.8	8.13	8.37

TABLE XXVI

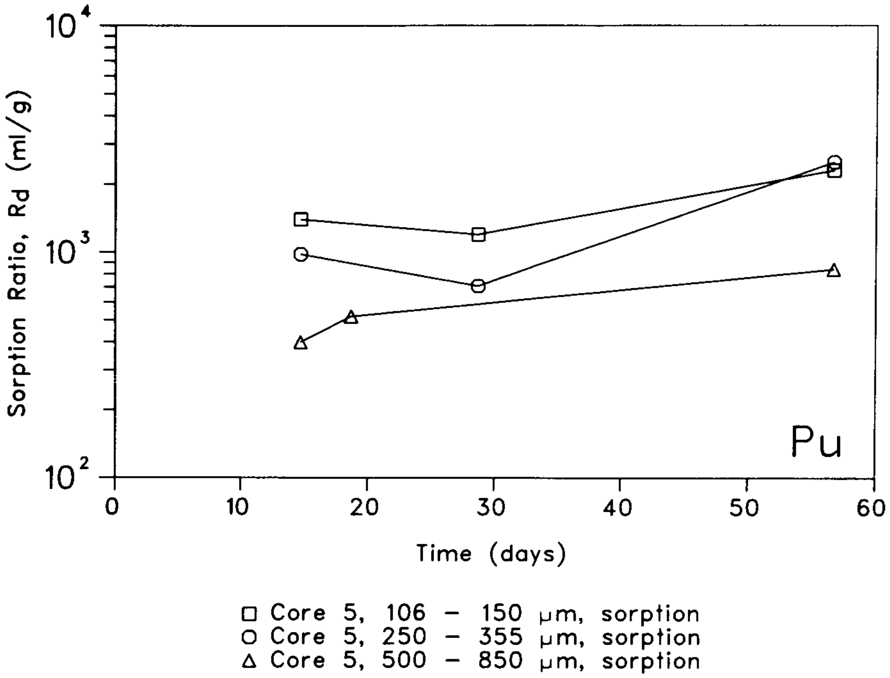
pH VALUES, SAMPLE CS5, 70°C

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	Initial pH	Final pH
106-150	7.7			8.29
		19.7	7.95	8.18
	14.7		7.98	8.12
	28.7		7.98	8.20
	56.7		7.98	8.36
		16.8	8.13	7.68
500-850	7.7			8.24
	14.7		7.98	7.79
	28.7		7.98	7.54
		15.7	7.95	8.33
	56.7		7.98	8.38

TABLE XXVII

pH VALUES, SAMPLE CS7, 70°C

Fraction (μm)	Sorption Time (days)	Desorption Time (days)	Initial pH	Final pH
106-150	7.7			8.35
	14.7		7.98	7.42
	28.7		7.98	
	56.7		7.98	
		16.8	8.13	7.45



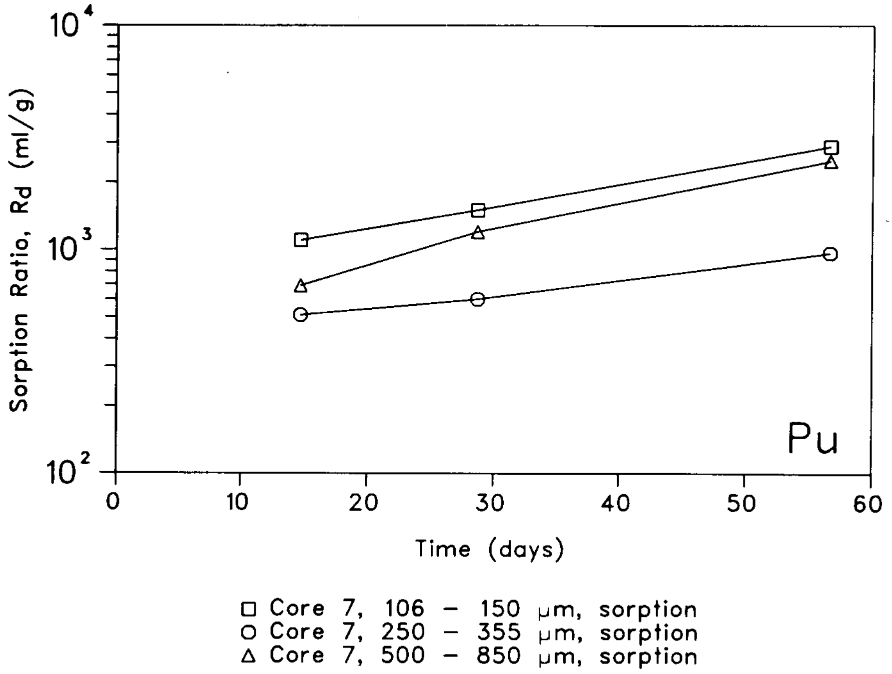


Fig. 21. Plutonium sorption-desorption ratio measurements, ambient temperature.

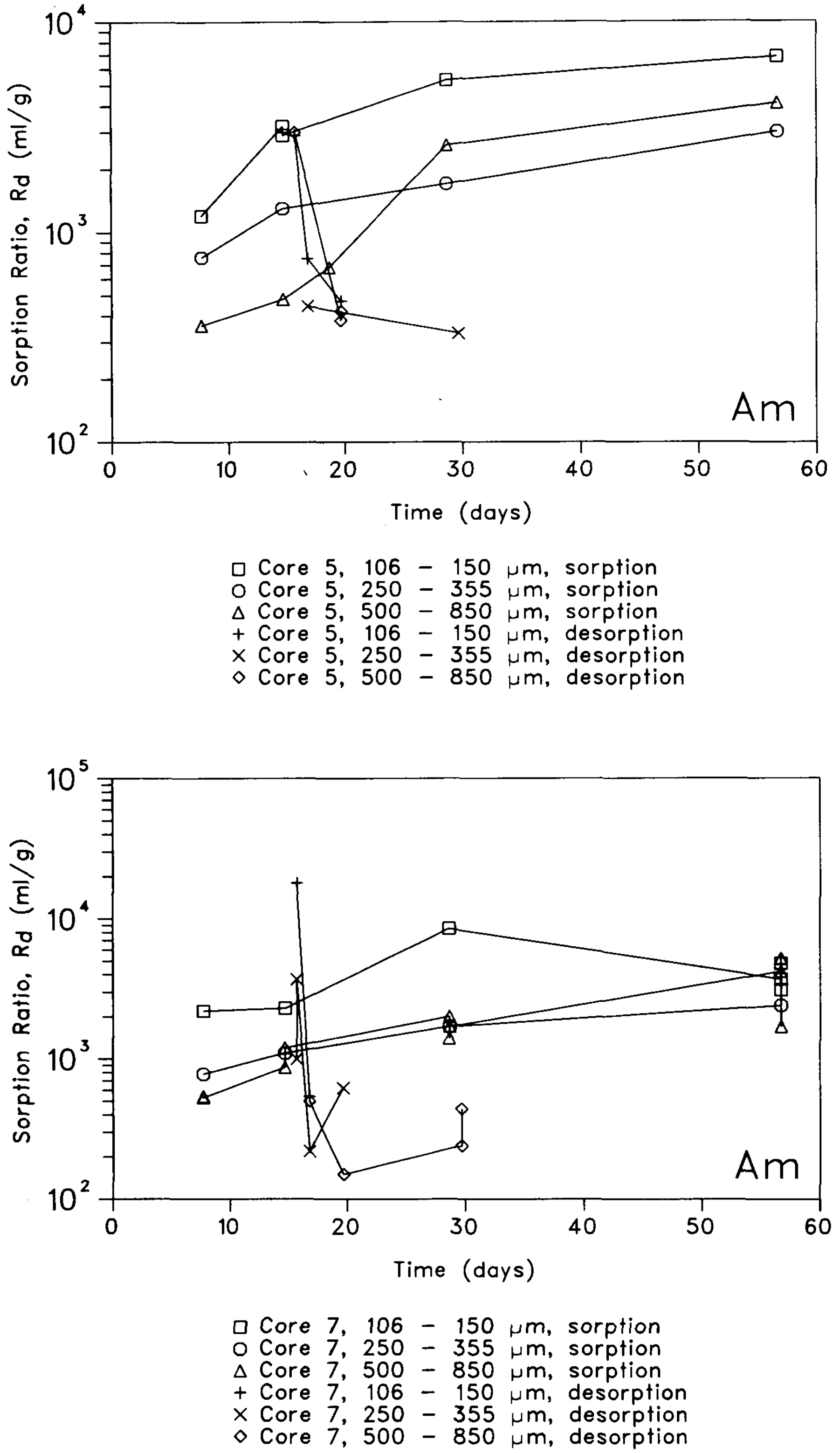


Fig. 22. Americium sorption-desorption ratio measurements, ambient temperature.

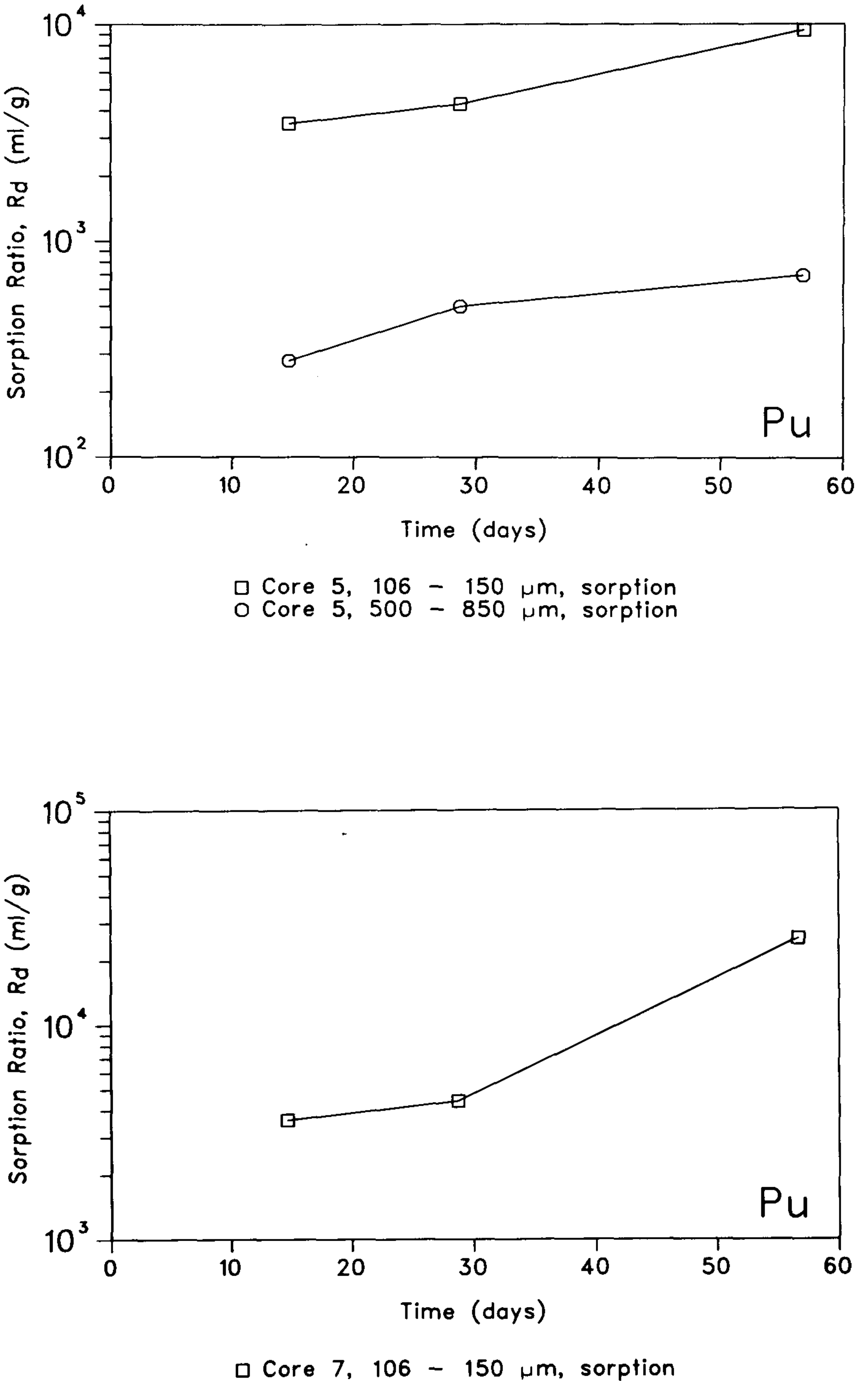


Fig. 23. Plutonium sorption-desorption ratio measurements, 70°C.

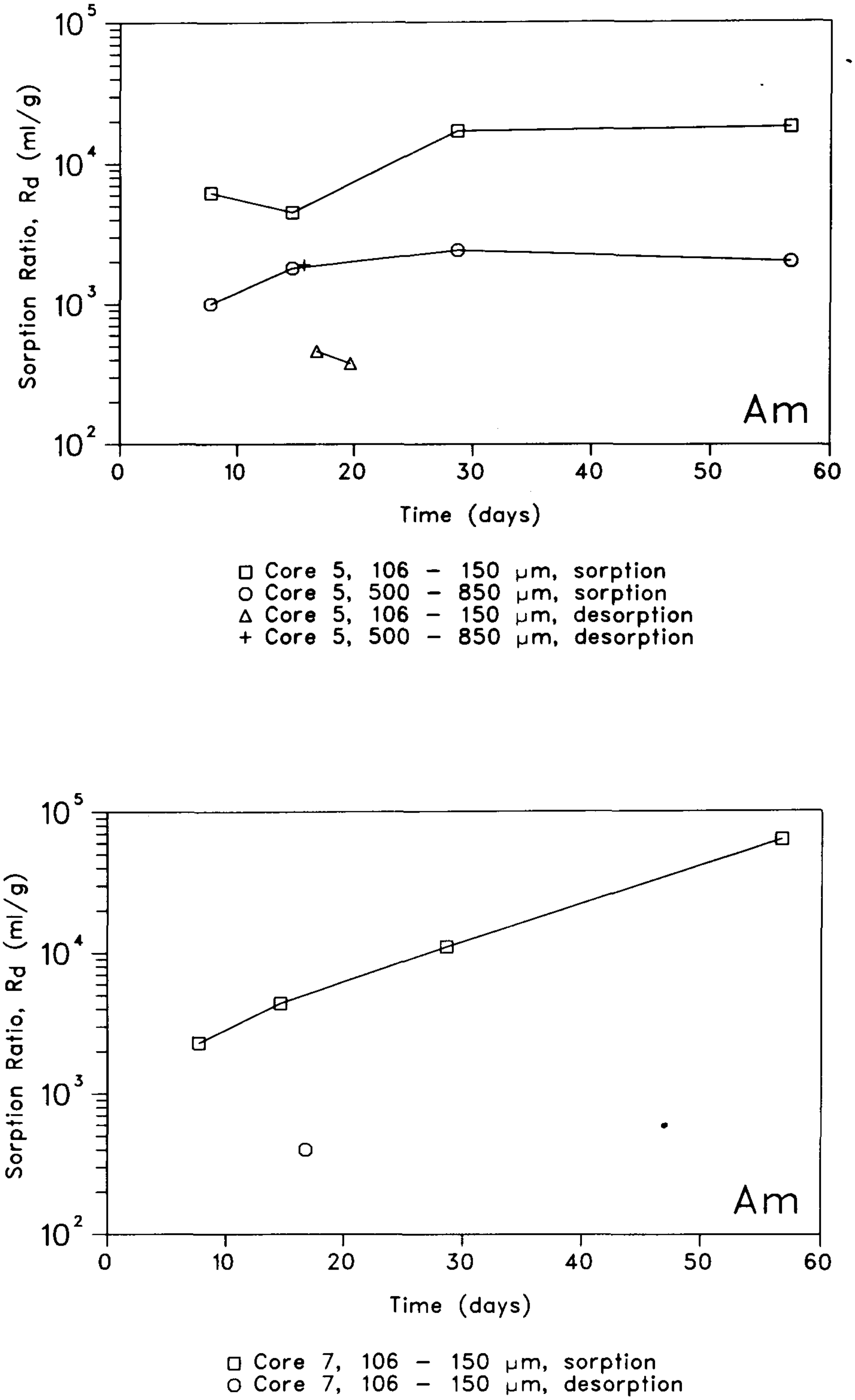


Fig. 24. Americium sorption-desorption ratio measurements, 70°C.

TABLE XXVIII
MEAN SORPTION RATIOS FOR Pu AND Am

			Sorption Ratio, R_d (mℓ/g)	
Element	Core	Temp. (°C)	Sorption	Desorption
Pu	CN5	22	1400 ± 420	
	CN5	70	3800 ± 3200	
	CN7	22	1600 ± 520	
	CN7	70	~ 15 000	
Am	CN5	22	3900 ± 1600	1000 ± 410
	CN5	70	10 000 ± 7500	1200 ± 740
	CN7	22	3700 ± 1600	3700 ± 3500
	CN7	70	~ 37 000	

Several general conclusions can be made for the Pu and Am results. At least qualitatively an increase in surface area is accompanied by an increase in sorption ratio. The R_d values increase with increasing temperature. Definitive conclusions cannot be made for the relationship of the desorption measurements to the sorption measurements.

VII. SUMMARY

Table XXIX summarizes representative sorption ratios for each of the elements studied at ambient (22 ± 2°C) and elevated (70 ± 1°C) temperature.

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TABLE XXIX
REPRESENTATIVE SORPTION RATIOS (mℓ/g)

	22 ± 2°C		70 ± 1°C	
Element	Sorption	Desorption	Sorption	Desorption
Sr	16±1	20±1	38±5	39±5
Tc(VII)	~30	~100	~10	~100
Cs	320±30	550±40	795±70	1370±240
Ba	164±25	170±30	718±240	750±230
Ce(III)	240±60	1410±270	41±5	1050±190
Eu(III)	550±150	1500±250	71±12	1160±140
U(VI)	4.4±1.0	15±2		
Pu	1500±330		a	
Am	3800±1100	1000±410	a	a

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[a] See Table XXVIII.

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