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CURRENT STATUS OF CRUSHED ROCK AND WHOLE ROCK COLUMN STUDIES

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ABSTRACT

Measurements on a large number of crushed rock columns of tuff, granite, and argillite are discussed. The isotopes ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, ^{152}Eu, ^{95m}Tc, and ^{233}U were used. Flow rates were varied from ~30 to ~3000 m/y. Other parameters studied include isotope concentration and atmosphere. The sorption ratios calculated were compared with batch sorption ratios on the same samples.

Methods of studying the movement of radionuclides through whole rock cores are described. The problems associated with sealing the cores to prevent leaking along the exterior surface and one possible solution are discussed. The strontium sorption ratio obtained by elution of one solid tuff core is compared with the batch and crushed rock column sorption ratios.

INTRODUCTION

The migration of radionuclides through crushed rock and whole rock columns was studied using granite, argillite, and tuff.[a] Although the tuff studies were mainly supported by the Nevada Nuclear Waste Storage Investigations program and the Radionuclide Migration Project, both managed by the Nevada Operations Office of the Department of Energy, they are included for completeness. The retardation factors, R_f, obtained on crushed rock columns were related to batch sorption ratios, R_d, by the simple equation $R_f = R_d (\rho/\varepsilon) + 1$ where ρ is the density and ε is the porosity.

Whole core columns, both intact and fractured, were studied primarily by sectioning the cores after some fraction of the activity was eluted and studying the distribution of activity with microautoradiography (MAR). A number of problems associated with running intact cores were identified.

DISCUSSION

Crushed Rock Columns

Simple, upward-flow, crushed rock columns were developed for migration rate studies. Each column was characterized in terms of the total column volume V (the size of the column calculated from column dimensions), the free column volume FCV (measured and used to calculate the effective column porosity), the column density, the particle size, and the flow rate. Flow rates were determined by weighing the eluate delivered in a known time period. Flow rates were relatively constant with a given syringe and pump (Sage Instruments, Model 352) setting and generally ranged from 0.041 to 0.082 mℓ/h. (A flow rate of 0.045 mℓ/h for a 2.1-cm-long by 0.5-cm-diameter column with a FCV of 0.224 mℓ corresponds to a flow velocity of ~37 m/y). In most cases the activity was loaded onto the column in a spike of a few μℓ.

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[a] Descriptions of the rocks used, Climax stock granite, Eleana argillite, and Yucca Mountain and Jackass Flats tuffs have been given in Erdal et al. 1979-1, Erdal et al. 1979-2, Vine et al. 1980 and Wolfsberg et al. 1979, respectively.

The FCV was determined with HTO and $^{131}I^-$. There was essentially no difference in the values obtained with HTO or with $^{131}I^-$ on any of the columns studied. A small retardation factor (2 to 6 mℓ/g) had been measured (Erdal, et al. 1980) for "iodide" on argillite, therefore, argillite columns CN-2#2 and CN-3 were run with both tritium and ^{131}I as well as technetium.

Preliminary investigations were made on several parameters. Flow rates were varied from 0.082 mℓ/h to 18 mℓ/h on three JA-32 tuff columns loaded with ^{85}Sr. Other fast flow columns were ^{137}Cs (spike) on tuff YM-38#3 run at ~4 mℓ/h and granite CS-5#2 loaded with ^{85}Sr, ^{137}Cs, and ^{133}Ba (spike) and run at ~5 mℓ/h. Argillite columns with ^{95m}Tc, ^{131}I, and HTO were run under controlled atmosphere conditions (≤0.2 ppm oxygen, ≤20 ppm carbon dioxide) as well as in air. The effect of the cesium ion concentration (10^{-6} to 10^{-9} M) on tuff was also investigated.

The calculated column sorption ratios for the isotopes ^{85}Sr, ^{137}Cs, and ^{133}Ba are given in Table 1 with data from batch sorption measurements (Vine et al. 1980, Erdal et al. 1979-1, 1979-2) for comparison. Several kinds of elution behavior were observed: symmetric peaks where fifty percent of the activity eluted corresponded closely to the peak of the elution curve, asymmetric peaks, and "no peaks" - but instead a slow, usually uniform elution of activity. In most cases the elution curves of ^{85}Sr fell into the first category, "symmetric peaks", with the column R_d value up to three times lower than the corresponding batch R_d value. Three JA-32 tuff columns were loaded with ^{85}Sr to compare the effect of varying the flow rate. The sorption ratios obtained on fast-flow column JA-32#2 and slow-flow column JA-32#3 agreed within ~5%. However, the fast-flow column was run with ^{85}Sr tracer added to the groundwater rather than loaded as a spike as on the slow-flow-rate column. A larger R_d was obtained on another spike-loaded column, JA-32#1. It was run by gravity flow which was often erratic and sometimes quite fast. With two granite columns, CS-5#1 and CS-5#2, both loaded with a spike of activity, a considerable increase in R_d was observed when the flow rate was increased from 0.04 mℓ/h (on CS-5#1) to 4.98 mℓ/h (on CS-5#2). Increases from 8.5 mℓ/g to 25 mℓ/g and from 32 mℓ/g to 165 mℓ/g were obtained for ^{85}Sr and ^{133}Ba, respectively. Only

TABLE 1

A Comparison of Batch and Column R_d Values

Column	^{85}Sr R_d (mℓ/g)		^{137}Cs R_d (mℓ/g)		^{133}Ba R_d (mℓ/g)	
	Batch	column	Batch	column	Batch	Column
Granite						
CS-5#1	14	29	347	>665[a,b]	154	32
CS-5#2[c]	14	25	347	"708"[b]	154	165
CS-7	18	15	568	(a,b)	175	44
Argillite:						
CN-1	138	43	1830	>570[a]		
CN-2#1	156	52	1580	>520[a]		
Tuff:						
JA-32#1[d]	55	56				
JA-32#2[c,e]	55	38				
JA-32#3	65	36				
YM-22	50	30	287	122	899	355
YM-54#1	84	44	247	92	620	126
YM-54#2[e]			247	80		
YM-54#3	84	44	247	113	620	122
JA-37	370	106	740	>560[a,b]		
JA-18#1	16000	381 (9%)[a]	6600-15000	(a)		
JA-18#3	16000	(a)	6600-15000	(a)	4800	(a)
YM-38#3[c]			8600	"21900"[b]		

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[a] In progress.

[b] Peakless elution.

[c] Fast flow.

[d] Gravity flow.

[e] Continuous feed.

a partial (peakless) elution has been obtained for ^{137}Cs on the slow-flow-rate column. A "peakless R_d" of 708 mℓ/g was obtained on the fast-flow column.

Column JA-18#1 was loaded with ^{85}Sr, for which a large batch R_d value (16000 mℓ/g) was measured. Five percent of the strontium on this column was eluted in ~72 days; then a small, sharp peak (R_d = 381 mℓ/g) containing 9% of the total activity was observed. Elution of the column continued after the peak was observed, and the slow, uniform "leaking" resumed. The JA-18 is a highly glassy tuff, and the slow elution may be due to a gradual dissolution of the glass. This, however, would not explain the weak, sharp peak, which seems to indicate that more than one "sorption" mechanism exists. The column was also loaded with ^{137}Cs, and the same slow "leaking", without a sharp peak, was observed. Besides dissolution of the glass, the slow elution of ^{85}Sr and ^{137}Cs might also be the result of exchange of the sorbed radioactive species with stable isotopes in the pretreated waters used, which contain ~10^{-9} M cesium and ~6 x 10^{-7} M strontium.

Other cesium column data are given in Table 1. Only on tuff columns of YM-54 (3 columns) and YM-22 (1 column), where the batch distribution coefficients are fairly small and values from desorption and sorption experiments are approximately equal, did the elution of activity occur in a peak. The YM-54 columns were run at two ^{137}Cs concentrations, 10^{-6} M and 10^{-9} M. No effect on the sorption ratio was observed. On granite columns CS-5#1 and CS-7 a slow elution of ^{137}Cs began at about day 48 and continued for more than one year. With fast-flow-column CS-5#2 (~5 mℓ/h), ^{137}Cs was also removed in a slow, peakless, elution. On the JA-37 column <5% of the total cesium was removed in ~30 weeks.

Another tuff (YM-38) was loaded with ^{137}Cs and run at 4-5 mℓ/h. The ^{137}Cs was detected at about 1150 mℓ. Fifty percent of the total ^{137}Cs was eluted in 7680 mℓ in slowly increasing amounts. (If the average flow rate used on the majority of columns had been used in this case about 29 years would have been required to collect the total of 10.5 ℓ eluted.) A peak was not observed, but a column "R_d value" of 21900 mℓ/g was estimated from the volume required to elute 50% of the activity. This is a value well above that obtained from batch measurements (8600 mℓ/g), is indicative of the "complications" revealed by flow experiments, and is probably due in part to the fast flow rate used.

All of the columns run to date with ^{133}Ba have shown peaks, although some were quite asymmetric. The column R_d values are given in Table 1; they are 2.5 to 4.8 times lower than the corresponding batch R_d value, except for CS-5#2, run at a fast flow rate, where the column R_d was 1.07 times higher than the batch R_d. The ^{133}Ba peak from CS-5#2 was also considerably broader than that from CS-5#1. Only materials with relatively low sorption ratios for barium have been used in columns. Thus, the more complicated situations, better revealed by high R_d values, were not studied with barium. On columns of YM-54 and YM-22 with batch R_d values of 620 and 899 mℓ/g, respectively, the batch sorption and desorption ratios were equal, implying a reversible interchange of ions. For "comparable" batch sorption R_d numbers with cesium on columns of granite, tuff, and argillite, simple peaks were not observed. The batch desorption R_d values were at least a factor of two larger than the sorption R_d values, which could suggest that more than one species and/or mechanism with different rates of reaction were present during sorption (and absent in batch desorption measurements) or that mineral alteration due to weathering in the batch studies affected sorption vs. desorption. For the granite columns (batch desorption values were about twice those for sorption) the peaks of the barium elution curves represented less than half of the total activity and were followed by a slow, uniform elution.

Other isotopes studied were ^{141}Ce, ^{95m}Tc, ^{237}U, and ^{131}I. Column JA-18#2 was loaded with ^{141}Ce and ^{152}Eu. In nine months $\leq$0.005% of the ^{152}Eu was eluted. Another tuff column, YM-54#4, was loaded with spikes of ^{131}I and ^{237}U simultaneously. Due to the small size of the columns, drop collection of the eluate was required. Since the drop rate was very slow, the drops partially evaporated on the column tip before collection. To prevent this the fraction collector and column were placed in a humidity box and a hot plate with a beaker of water was placed inside the box to maintain ~100% humidity. The loss of iodide when it was dried (with ^{237}U) in carrier free form was a problem until "fixers" were used. Filter paper disks at the bottom of the collection planchets were pretreated with 100 µℓ $NaHSO_3$ (~1 mg) and 100 µℓ NaI (~2 mg) and air dried. After sample collection, 50 µℓ (~0.5 mg) $NaNO_3$ was added before air drying. The fixers made very stable samples which had good reproducibility. Column YM-54#4 gave an R_d value of 0.72 mℓ/g for uranium, compared with an average batch R_d value of 1.5 mℓ/g. The uranium peak was quite asymmetric. Again, the marked asymmetry could be an effect of the complicated "sorption" illustrated by the large difference between batch sorption (1.5 mℓ/g) and desorption (11 mℓ/g) ratios.

With technetium, breakthrough curves were obtained simultaneously with tritium and ^{131}I on argillite CN-2#2 (atmospheric conditions) and argillite CN-3 (controlled-atmosphere conditions, $\leq$0.2 ppm oxygen and $\leq$20 ppm carbon dioxide). The ^{131}I and HTO gave identical breakthrough curves, indicating no retardation of iodide on argillite, as was previously indicated by batch measurements (Erdal <u>et</u> <u>al</u>. 1980). The column R_d values for ^{95m}Tc, 0.4 mℓ/g on CN-2 and 0.3 mℓ/g on CN-3, were considerably less than those obtained by batch techniques: 30.5 mℓ/g for CN-2 in air and 175 mℓ/g for CN-3 in the controlled atmosphere. However, the columns were run at a fast flow rate (~2 mℓ/h), reducing the time of contact between technetium and the rock by 80 to 700 times that of the batch measurements. This could also explain the apparant lack of effect of the ≤0.2 ppm oxygen atmosphere; the fast flow rate would limit the time available for reduction of pertechnetate. Since the sorption of technetium on argillite has been shown to be strongly time dependent (Daniels et al. 1980), particularly with ≤0.2 ppm oxygen, the difference between batch and column R_d values is probably reasonable.

Whole Core Columns

Because studies using crushed rock involve mineral surfaces newly exposed to the atmosphere and to water and those utilizing geologic thin-sectons involve surfaces exposed and possibly altered by grinding and polishing, experiments were started with intact rock cores. Such measurements should provide a better understanding of the transport of radionuclides through rock, either by porous or fracture flow. In addition, they are an intermediate step in the extrapolation from batch and crushed rock column studies to the field.

Several experiments using solid rock cores were completed. The equipment used in these experiments is essentially the same as that described in Erdal et al. 1979-3 and Vine et al. 1980. Cylindrical core samples 15.9 mm high and 25.4 mm in diameter were placed in Teflon sleeves with porous disks of pressed stainless steel on each end. Steel cylinders of the same diameter as the sample, with pressure lines attached, were inserted into the ends of the Teflon cylinder before placing the assembly in a vessel which could be pressurized. Stainless steel capillary tubing led to the collecting tube. Pretreated groundwater was forced through the core by a "driving" pressure significantly lower than the confining pressure. After the core had been flushed with groundwater it was removed, loaded with a "spike" of activity, and again placed in the pressure assembly.

A summary of the cores studied is given in Table 2. The majority of cores were studied using microautoradiography after they were sectioned with a rock saw. The only core for which an "elution curve" was obtained was tuff YM-22. In one year ~40% of the ^{85}Sr was removed at a fairly

TABLE 2

Intact Core Columns

Core	Isotope	Flow rate[a]	Activity Removed	Comment
YM-22	^{85}Sr	0.8 mℓ/d (1 yr)	~40%	"Peakless" R_d ~25 mℓ/g; batch ~50 mℓ/g
YM-45	^{241}Am	0.8 mℓ/d (5 wk)	0.2%	Used for MAR, evidence of leaking between Teflon sleeve and core
Climax Stock C-79-5b-1	^{241}Am	0.2 - 4 mℓ/d	~2%	Fractured; used for MAR; evidence of leaking between Teflon sleeve and core
YM-54-a-1	^{233}U	1.5 mℓ/d	trace	Epoxy coated; used for MAR
Climax Stock C-79-9b-1	^{233}U	0.1 mℓ/d (1d)	~3%	Fractures; epoxy coated, used for MAR
JA-35	^{233}U	0.1 mℓ/h		Epoxy coating cracked
YM-54-a-3	^{233}U	0.1 mℓ/h (26h)	trace	Top face of core grooved, epoxy penetrated end cap; used for MAR

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[a] Number in parentheses is length of time core was eluted.

constant, "peakless," rate. A rough value of ~25 mℓ/g was estimated for the sorption ratio. This is less than the value obtained from batch measurements ~50 mℓ/g (E. N. Vine <u>et al</u>. 1980), and similar to the value of 30 mℓ/g obtained on a crushed rock column of YM-22 (see Table 1).

Data from two cores, tuff YM-45 and Climax Stock granite, both loaded with ^{241}Am, suggested that there was leakage of pumped water between the Teflon sleeve and the core surface. Low to moderate levels of activity were found on the bottom and sides of core YM-45. (The majority of the activity loaded remained on the top core face and metal end cap.) Using MAR with Kodax NTB emulsion and "Ultrafilm-H" showed that ^{241}Am was deposited primarily in an aggregated form; there was a high ratio of stars to single tracks and one large colloid was observed on the bottom surface.

To try to eliminate the leakage problem, several cores were coated. One core, coated with a thin layer of polyurethane prior to inserting in the Teflon sleeve, was also fitted with polyethylene washers and end caps. Substantial amounts of activity were still found on the exterior surfaces. It was not clear whether this was due to leakage from the top flow through surface areas not completely coated with polyurethane, or simply penetration by alpha particles of the very thin coating. Another core, along with both end caps, was cast in polyurethane. No leakage was observed around the end caps, and the rock-to-resin bond seemed to maintain its integrity.

A Buehler epoxy has since been used for encasing cores. Experiments were performed to measure the extent of penetration of the epoxy into the core (which might inhibit water flow) and to determine if the activity sorbed in regions of the core containing epoxy. (Batch R_d values with this epoxy for a 7-day contact time were ≤ 1 mℓ/g for ^{85}Sr, ^{137}Cs, and ^{133}Ba, 17 mℓ/g for ^{152}Eu, and 1010 mℓ/g for ^{141}Ce.) Elution of tuff core YM-54-a-1 with ^{233}U loaded in the center of a washer was stopped when ^{233}U was detected in the effluent. Counting and MAR showed ^{233}U had penetrated ~5 mm into the core and remained concentrated in the center of the core.

A fractured granite core, loaded with ^{233}U was also stopped after elution of a small fraction of the activity. The whole core was counted in a NaI(Tl) well counter, then sectioned with a rock saw. The polyethylene washer confined most of the activity to the top center of the core face; however, this pattern of activity was not maintained down into the core. The activity levels on the interior surfaces of slices taken through the core were very low. A system of cracks over about 25% of the slice area seemed to be responsible for all of the flow. There was no indication that the epoxy had penetrated appreciably into the core, nor were there regions of high track density near the core-epoxy interface.

CONCLUSIONS

A large number of crushed tuff, granite, and argillite columns have been studied. At flow rates of ~30 m/y, column R_d values (when peaks are observed) are generally lower than those obtained with batch measurements. If flow rates are increased to as much as 3000 m/y, R_d values for columns loaded with spikes of activity also increase, becoming equal to or larger than batch R_d values. Except in the simplest of cases, where sorption coefficients are relatively low, and ion-exchange equilibria not only exist but are the dominant mechanism for removal of radioisotopes from solution, the simple relation between the distribution coefficient K_d or R_d and the relative velocity of radionuclides with respect to the water velocity may be insufficient to permit accurate modeling of the retardation of radionuclides. Thus, the mechanisms causing retardation need to be studied in order to understand the relationship between behavior in a dynamic laboratory experiment (and, ultimately, behavior in the field) and the many available batch R_d data.

One solid tuff column gave a sorption ratio for strontium similar to that obtained on a crushed rock column with the same tuff. Both values were lower than the corresponding batch R_d.

Progress has been made toward development of a method for encasing whole rock cores in a material such as epoxy so that flow down the walls is prevented. This approach should greatly increase the number of measurements which can be made because, at least for permeable rocks, it obviates the need for confining pressure and, therefore, the pressurized-core apparatus. Further development of such techniques is now in progress.

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