

Migration Behaviour of Barium and Strontium in Granite

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Summary

The sorption behaviour of Ba²⁺ and Sr²⁺ cations on granite have been studied under flowing and static conditions in column and batch experiments. ¹³³Ba, ⁹⁰Sr and ³H were used as radio tracers. The retardation factors, R_f , and distribution ratios, R_d , of barium and strontium in column experiments were found to be smaller than those from batch experiments. In both techniques barium was sorbed more strongly on granite than strontium. Sorption energies were found to be in good agreement with literature values.

Introduction

Geological matrices surrounding a waste repository are expected to act as natural barriers to both water flow and radionuclide migration, since many radionuclides sorb strongly on clays and rocks. Several such sorption studies are reported in the literature [1–14]. Granite, the most common igneous rock which consist of orthoclase, quartz and muscovite appears to be an excellent candidate for a repository area. The general formula of these constituent minerals are as follows [15]:

Orthoclase: K (AlSi₃O₈)

Quartz: SiO₂

Muscovite: KAl₂ (AlSi₃O₁₀) (OH)₈

Information about granite's sorption capacity can be obtained via batch and column experiments.

In batch experiments, the distribution ratio, R_d , which expresses the concentration of the sorbed cation on the solid phase to that in the aqueous phase were calculated from the measured initial and final activities using equations given elsewhere [16].

In column experiments migration of a radionuclide is characterized by a retardation factor, R_f , which is related to the average radionuclide velocity (V_f) – migration rate – in the matrix with respect to the average water velocity (V_w) in the same medium. The column R_d values can be extracted from R_f 's using the relation:

$$R_f = 1 + R_d \frac{r_s A_c u_w}{w} \quad (1)$$

where,

r_s : Density of solid matrix (g/cm³)

A_c : Cross sectional area of the column (cm²)

u_w : Pore water velocity (cm/h)

w : Volumetric flow rate of water in the column (cm³/h)

The results of batch and column experiments lead to information on the type of sorption process, sorption energies and the parameters affecting retardation.

Among the several fission products which are discharged into the environment, ⁹⁰Sr ($t_{1/2} = 28.8$ y) is important because of its high fission yield and long half-life. Another product with a high fission yield is ¹⁴⁰Ba ($t_{1/2} = 12.8$ d), a safety hazard during the first hundred days of its release. Furthermore barium is a homolog of radium, an important radioelement in radioactive waste considerations. Barium studies therefore can be used as an analogue to radium. Presumably, if granite has a high sorption capacity for these radionuclides, then it can be used as a host rock in radioactive waste deposition.

In this work the sorption behaviour of Ba²⁺ and Sr²⁺ cations on granite has been studied by employing both batch and column techniques. ¹³³Ba, ⁹⁰Sr and ³H were used as radiotracers.

Experimental

The column and batch experiments were carried out at room temperature. ¹³³Ba, ⁹⁰Sr and ³H radionuclides which were obtained from the Radiochemical Center, Amersham were used as tracers. The solid matrix granite was obtained from deposits of Central Anatolia. Fourier transform infrared (Fig. 1), X-ray diffraction (Fig. 2) and differential thermal gravimetric analysis studies were carried out to elucidate the structure of granite matrix. Particle size fractionation gave a weighed average particle size of 161 μm and surface area measurements indicated 0.75 m²/g specific surface area.

All solutions were prepared using synthetic groundwater with a composition similar to the groundwater around the granite deposit. The composition of the synthetic groundwater is given in Table 1.

In column experiments, retardations of radionuclides were determined by measuring the effluent activities collected from the bottom of a mini-column system which was 0.32 cm in diameter and 28.7 cm in height (Fig. 3). The column was packed with a weighed amount of granite powder. After four days of

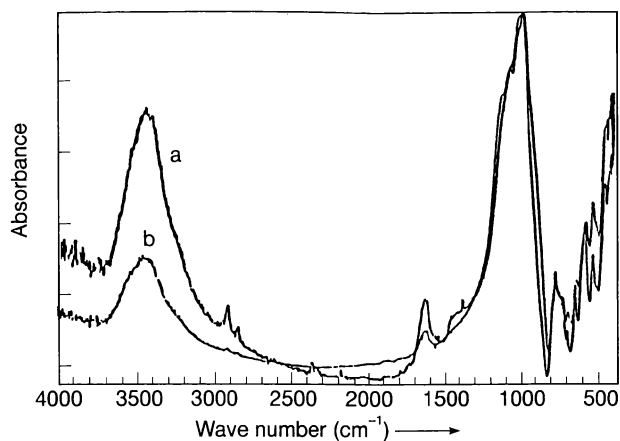


Fig. 1. Fourier transform infrared spectra of: a U.S. Geological Survey Standard Granite, b Granite used in experiments.

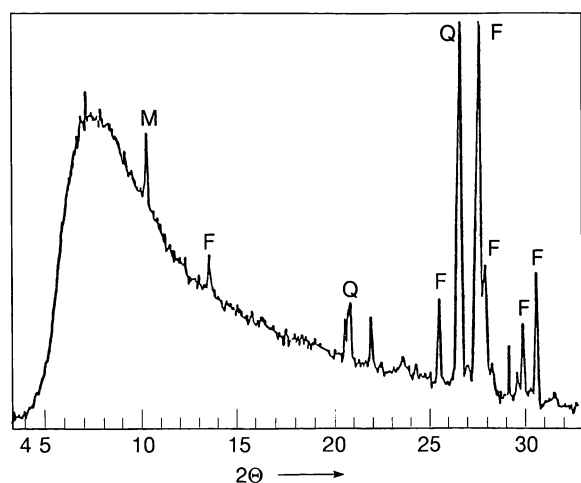


Fig. 2. XRD-traces of granite, (Ni filtered CuK_α radiation). M: Mica, F: Feldspar, Q: Quartz.

Table 1. Composition of synthetic groundwater used in the sorption experiments

Ion concentration (meq/mL)								pH
Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	CO ₃ ²⁻	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	
0.89	0.89	4.70	3.15	0.17	3.14	0.84	0.18	7.80

pre-equilibration with groundwater a spike of radionuclide solution was introduced from the top of the column by injection. The migration of the radionuclide of interest through granite matrix was then initiated with a continuous water flow through the column and the fractions of active solutions passing through the column were collected by a fractional collector at specific time intervals. The water flow rate for barium experiments was 2.1 mL/h and that of strontium was 3.4 mL/h. The activities of the solution samples were determined by γ -ray spectroscopy (^{133}Ba), by liquid scintillation counting (^3H) or by β -counting (^{90}Sr).

The activities of effluents collected at certain time intervals were normalized as the fraction of initial total

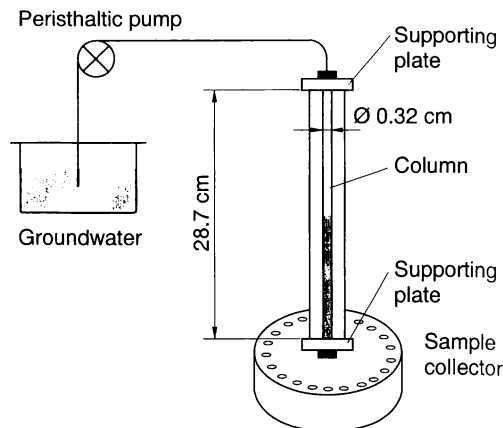


Fig. 3. Mini-column system used in column experiments.

activity. The breakthrough curve of each column experiment was drawn by plotting normalized activities as a function of time. The travelling times of radionuclides obtained from these curves were used to extract the transport velocity of the radionuclide in the granite matrix.

The average water velocity in the same matrix, a necessary parameter in the calculation, was obtained by performing similar column experiments with tritium solutions. Tritium was considered to be a nonadsorbing tracer.

In batch experiments, weighed amount of solid samples were shaken with known volumes of radioactive barium and strontium solutions for certain times. A lateral shaker was used at a rate of 250 rpm. Initial cation concentrations before sorption ranged from 10^{-8} mol/L to 10^{-2} mol/L. After separation of the two phases by centrifugation and filtration, the change of adsorbate activity in the aqueous phase was measured and the distribution coefficients were calculated.

Results and discussion

Typical breakthrough curves obtained in the column experiments of barium-granite and strontium-granite interactions are shown in Fig. 4 and 5 respectively. In Fig. 6 the breakthrough curve of tritiated water is shown. Contrary to the tritium breakthrough curve, tailings were observed to the right of the peaks in barium and strontium curves. This observation is characteristic of chromatographic processes where adsorption is the dominant mechanism leading to retardation.

The velocities of barium, strontium and tritium movements along the column were obtained by dividing the matrix depth with retention times in each column. The retardation factors (R_r) and the distribution ratios (R_d) were calculated accordingly. The results obtained are given in Table 2.

In batch sorption experiments, kinetic studies indicated that saturation was reached in about fourteen-days in both barium-granite and strontium-granite in-

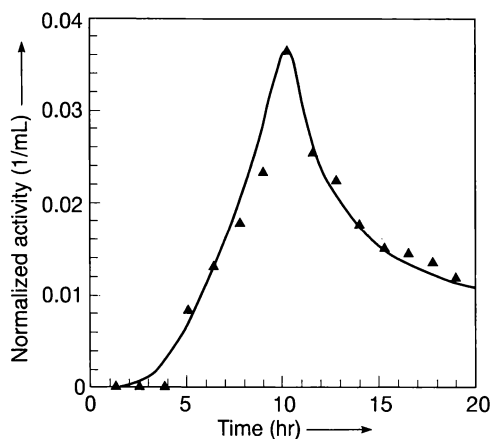


Fig. 4. The breakthrough curve obtained from barium-granite column experiments. Matrix depth: 8.0 cm. \blacktriangle Normalized activity versus time.

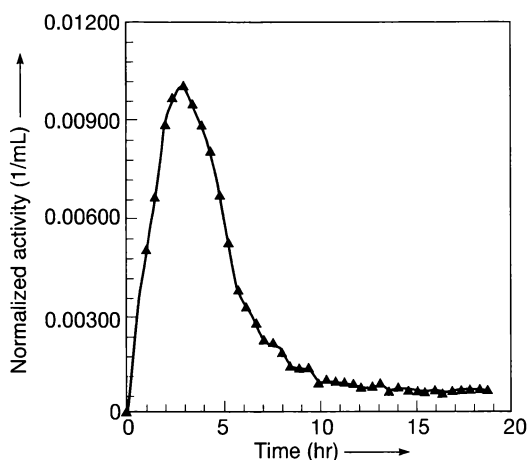


Fig. 5. The breakthrough curve obtained from strontium-granite column experiments. Matrix depth: 5.0 cm. \blacktriangle Normalized activity versus time.

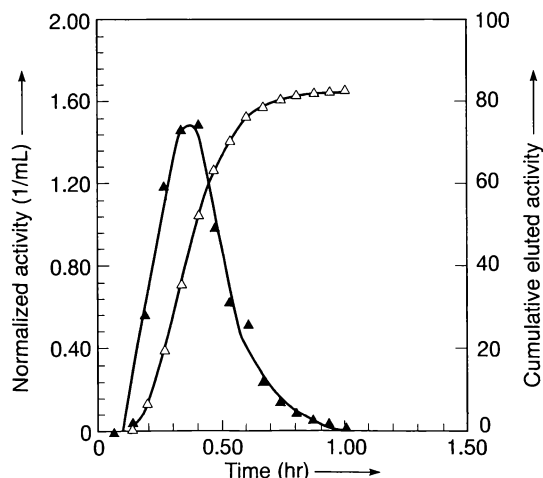


Fig. 6. The breakthrough curve obtained from tritium-granite interactions. Matrix depth: 7.8 cm. \blacktriangle Normalized activity versus time. \triangle Cumulative eluted activity percent versus time.

Table 2. Results of column and Batch experiments for Ba-granite Sr-granite interactions

Radionuclide	R_f	R_d (mL/g) (Column)	R_d (mL/g) (Batch)
Barium	37 ± 3	18 ± 2	700 ± 138
Strontium	26 ± 2	12 ± 1	100 ± 35

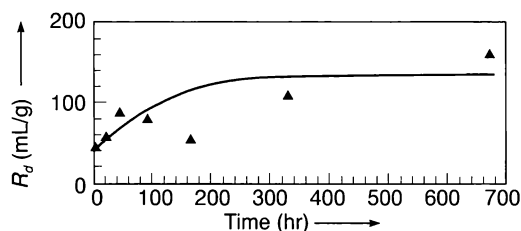


Fig. 7. The time evolution of Sr^{2+} ion sorption on granite.

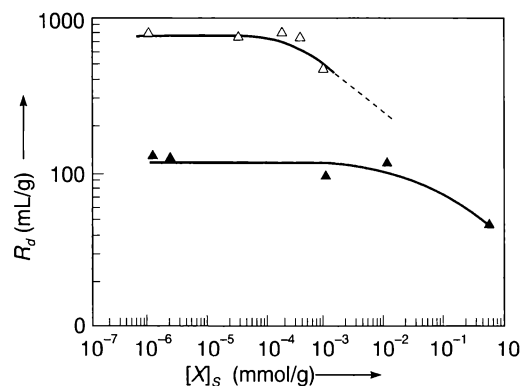


Fig. 8. The change of R_d values as a function of cation loadings. \triangle Ba^{2+} loading. \blacktriangle Sr^{2+} loading.

interactions. The time evolution of Sr^{2+} ion sorption on granite is illustrated in Fig. 7.

The variation of the distribution ratios, R_d , as a function of Ba^{2+} and Sr^{2+} ion concentration on the solid phase are shown in Fig. 8. It is seen that the R_d values were not strongly dependent on barium loadings in the 10^{-6} mmol/g– 10^{-4} mmol/g range. An average saturation R_d value of 700 mL/g was determined. A sharp decrease in R_d values observed above 10^{-4} mmol/g may be due to the near complete saturation of available adsorption sites. In the case of strontium sorption, R_d values were found to vary slightly in the 10^{-6} mmol/g– 10^{-2} mmol/g Sr^{2+} ion loading range. An average R_d value of about 100 mL/g was determined in this case (Table 2).

The experimental data obtained in the batch experiments were fitted to various sorption isotherm models. They were found to be best described by Freundlich [17] and Dubinin-Radushkevich [18] type isotherms. The isotherm parameters obtained are given in Table 3.

Using these parameters the corresponding empirical Freundlich isotherm for barium-granite sorption system may be expressed as:

Table 3. Various parameters obtained in fitting of the experimental sorption data to isotherm models

Isotherm model	Parameter	Ba ²⁺	Sr ²⁺
Freundlich	<i>K</i>	285	43
	<i>N</i>	0.95	0.94
Dubinin-Radushkevich	<i>X_m</i> (mol/g)	1.1 × 10 ⁻⁵	4.39 × 10 ⁻⁴
	<i>K</i> (mol ² /kJ ²)	4.51 × 10 ⁻³	6.26 × 10 ⁻³
	<i>E</i> (kJ/mol)	10.5	8.9

$$R_d = 285 [\text{Ba}]_i^{-0.05} \quad (2)$$

Here $[\text{Ba}]_i$ is the concentration of Ba²⁺ in the solution following sorption. The corresponding expression for the strontium-granite sorption becomes

$$R_d = 43 [\text{Sr}]_i^{-0.06} \quad (3)$$

In the case of the Dubinin-Radushkevich type isotherm the empirical relationships can be expressed as

$$R_d = 1.1 \times 10^{-4} [\text{Ba}]_i^{-1} \exp[-4.5 \times 10^{-3} (RT \ln(1 + [\text{Ba}]_i^{-1}))^2] \quad (4)$$

for barium sorption and

$$R_d = 4.39 \times 10^{-4} [\text{Sr}]_i^{-1} \exp[-6.26 \times 10^{-9} (RT \ln(1 + [\text{Sr}]_i^{-1}))^2] \quad (5)$$

for strontium sorption.

The sorption energy, *E*, was found as 10.5 kJ/mol for barium and 8.9 kJ/mol for strontium-granite interaction (Table 3). These are in good agreement with the literature range of 8–16 kJ/mol assigned to surface adsorption reactions [19].

To conclude, following observations can be underlined:

Both in the barium-granite and strontium-granite sorption studies the *R_d* values found from batch experiments were much larger than those from the column experiments. Namely 700 mL/g and 18 mL/g for barium and 100 mL/g and 12 mL/g for strontium sorptions respectively. This may result from the longer radionuclide-granite interaction times employed in the batch experiments, with the mica fraction in granite being responsible for the observed higher adsorption.

In both cases, the magnitude of the sorption energies suggest that the sorption process is mainly a surface phenomena. A fact which is also supported by the magnitude of isotherm parameters.

Retardation of barium is found to be greater than strontium, which indicates that granite formations are

suitable disposal site particularly for radiobarium containing nuclear waste.

Acknowledgements

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