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PRELIMINARY RESULTS OF EXPERIMENTAL WORK IN THE RADIONUCLIDE MIGRATION PROGRAM

The Sorptive Character of Tuffaceous Rocks in a "Static" versus "Dynamic" Mode of Testing

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INTRODUCTION

Underground nuclear testing and the subsurface disposal of radioactive waste products from nuclear power reactors introduce radioactive ionic species into ground water regimes. Ionic species, radioactive or stable, are selectively removed from solution during the flow of groundwater through permeable rocks via ion exchange reactions between the mineral surfaces and the aqueous solution. The factors which affect the efficiency of an ion exchange reaction are ionic concentration, the nature and concentration of competing ions, the chemical nature and surface area of the mineral exchange medium and the pH of the solution.

Laboratory measurements of the distribution of ions between an exchange medium and the coexisting solution are commonly conducted under "static" conditions by means of the batch method (see Fig. 1a). The term "static" denotes the fact the solution is in contact with the exchange medium but there is no semblance of dynamic flow of the solution through the exchange medium as occurs in groundwater systems.

PURPOSE AND SCOPE

This experimental study was conducted for the purpose of measuring the distribution of ionic species between an exchange medium and an aqueous solution under dynamic or flow conditions (see Fig. 1b). Corresponding static experiments were conducted in order to provide a basis for evaluation of the dynamic scheme. The experimental work was planned so as to begin with relatively simple experiments and proceed to more complicated ones. The work reported here was designed to measure the sorptive capacity of various exchange media with respect to a specific cation, i.e. Sr^{++} . It was not the intention to examine specific ionic exchange equilibria during this phase of the study, thus no competing ions were added to the solutions. Ion exchange equilibria in a dynamic mode of testing will be examined in future studies.

FIG. 1A

THE STATIC OR BATCH METHOD FOR TESTING THE SORPTIVE CHARACTERISTICS OF ROCK IS COMMONLY USED IN LABORATORY STUDIES

1. A solution containing the ion(s) of interest is added to a powdered rock sample.
2. Sample is agitated and centrifuged.
3. Samples are taken through time and ion concentration of solution is compared to original concentration to determine amount of ion sorbed.

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FIG. 1B

THE DYNAMIC OR FLOW MODE OF TESTING MORE CLOSELY REPRESENTS SORPTION PHENOMENA IN GROUND WATER SYSTEMS

1. Whole rock core is placed in confining cylinder.
2. Solution containing ion of interest is forced through core.
3. Ion concentration in filtrate is compared to original concentration to determine amount of ion sorbed by core.

STATIC EXPERIMENTS

MATERIALS

Sorption experiments in the static mode were carried out with a number of different volcanic rocks from NTS. In Table 1, an annotated list of samples is presented. The most extensive static testing was done with rock from the Trailridge Member of the Thirsty Canyon Tuff because of its combination of good sorptive and permeability characteristics.

The source of Sr^{++} ion in the solutions used for static and dynamic testing was from a combination of strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) and strontium oxide (SrO). A pure ($\text{Sr}(\text{NO}_3)_2$) solution in deionized water was considered unsuitable due to its relatively low pH of 5.5 (the pH of the deionized water alone). The SrO solution resulted in a pH of ~ 11 . By using both components in the same stock solution, the pH could be adjusted to any value in the range from 5.5 to 11.5.

METHOD

A number of different combinations of rock mass, solution volume and cation concentration were evaluated in the static mode of testing before adopting a scheme of 0.5 grams of rock, 25-30 ml of solution with an initial concentration of ~ 40 ppm Sr^{++} ion. Rocks were crushed mechanically and manually and two grain sizes were used in the static experiments. The coarse particles used were < 8 mesh and > 14 mesh, i.e., between 1.4 and 2.4 mm diameter (very coarse sand). The fine-grained rock used was < 170 mesh or smaller than 0.088 mm in diameter (silt size).

The crushed rock was placed in a 40 ml polyethylene centrifuge tube, the solution was added, and the tube was manually agitated for about one minute initially and after each sample was taken. One to two ml samples were pipetted from the container after centrifuging at 10,000 rpms for ten minutes. Several samples were taken during each static run, ranging in time from a few minutes to 200 hours after the start time.

TABLE 1
ROCK SAMPLES USED IN STATIC EXPERIMENTS

Rock Unit	Source	Lithologic Description	Remarks
Tunnel Beds (Tibr)	Core from "T" tunnel on Rainier Mesa (U12T1, 362.8- 364.0)	Zeolitized bedded tuff	Good sorptive characteristics but rock disintegrates to mud when put in water.
Tunnel Beds (Tibr)	Core from UG-1 exploratory hole on Rainier Mesa (UG-1, 323.7)	Zeolitized bedded tuff.	Good sorptive characteristics. 12 micro- darcy permeability made the rock unsuitable for dynamic testing.
Spearhead member of the Thirsty Canyon Tuff (Ttsr)	Sample taken from outcrop on Pahute Mesa	Rhyolitic ash-flow tuff	Poor sorptive characteristics
Ammonia Tanks mbr. of the Timber Mt. Tuff (Tma)	Sample taken from outcrop on Pahute Mesa	Partially welded ash-flow tuff.	Poor sorptive characteristics
Trailridge mbr. of the Thirsty Canyon Tuff (Ttt)	Sample taken from outcrop on Pahute Mesa	Partially welded silicic ash-flow tuff (see Fig. 2)	Moderate sorptive characteristics and millidarcy range permeability.

THIN-SECTION OF THE
TRAILRIDGE MEMBER
OF THE THIRSTY CANYON
TUFF (Ttt)

FIG. 2

STATIC EXPERIMENTS cont'd

RESULTS

The results of the static experiment are depicted graphically in Figures 3a-c. In Figure 3a, the effect of rock-type, i.e., mineralogy, on sorption is shown. For the rocks tested, it appears that the amount of sorption is directly proportional to the zeolite content.

In Figure 3b, the effect of particle size, i.e., surface area is shown. The fact that the finer grain size shows greater sorption indicates, as expected, that adsorption plays a significant role in the overall sorption process.

In Figure 3c, the effect of pH on sorption is shown. When solutions of low pH are used in sorption experiments, the hydrogen ion (H^+) is a competitor for sorption sites and therefore results in less Sr^{++} ion being taken up by the rock. The effect of agitation on sorption can also be seen in Figure 3c. In the upper curve, the sample was agitated frequently and many samples were taken over a short period of time at the beginning of the experiment. The effect of greater shaking appears to have had the effect of making the system come to equilibrium more quickly.

Two features of the plots in Figure 3b and 3c should be noted. First, the curves tend to be flat-topped, i.e., equilibrium appears to be achieved abruptly rather than gradually. Second, a maximum in the sorptive capacity occurs in a relatively short time and then there is a small tendency for the Sr^{++} ions to come off of the rock and return to the aqueous phase with time. Both of these features are significant and will be discussed in a later section.

THE EFFECT OF ROCK-TYPE ON SORPTION

FIG. 3A

THE EFFECT OF GRAIN SIZE ON SORPTION

FIG. 3B

THE EFFECT OF pH ON SORPTION

FIG. 3C

DYNAMIC EXPERIMENTS

MATERIALS

Rock cores used in the dynamic mode of testing have come from the Trailridge Member of the Thirsty Canyon Tuff (Ttt). Cores used in testing are 47.6 millimeters in diameter and have ranged from 25 to 50 millimeters in length. The aqueous solutions used for dynamic testing are identical to those used in the static experiments.

METHOD

The apparatus used for dynamic testing is of a very simple design. It consists of a stainless-steel closed cylinder which is connected to a solution reservoir which, in turn, is connected to a compressed-gas cylinder (see Fig. 4). The rock core is attached to an aluminum sleeve with epoxy, O-rings are fitted, and the sleeve is placed in the stainless-steel cylinder. The 40 ppm Sr^{++} solution is added to a 1500 ml reservoir and a small argon pressure is put on the solution to enhance the flow thru the core. The flow rate was set at ~ 5 ml/hour and samples were recovered on a daily basis.

RESULTS

The results of the dynamic experiments are shown in Figs. 5a-b.

Fig. 5a shows the results of a dynamic experiment with a 71.9 gram core of Ttt. The input solution had a pH of 7 and corresponded to the solution used in static experiments depicted in Fig. 3b. The two points on the curve indicate the amounts of strontium sorption expected on the basis of the coarse-grained and fine-grained static experiments. It is evident that sorption is considerably enhanced in the dynamic mode.

The experiment depicted in Fig. 5b was done with a 114.2 gram core of Ttt and a Sr^{++} solution of pH = 10. Again the two points on the curve show the amount of sorption expected on the basis of the corresponding static experiments (Fig. 3c, open circles). Note that this experiment was terminated prior to saturating the core with strontium due to difficulty experienced in maintaining the solution at a stable pH (the pH of the input solution underwent a gradual decline from 10 to 6.5 beginning at the two liter mark). Even though the sorption of Sr^{++} was diminished by the drop in pH, it is clear that there was a greater degree of sorption in the dynamic mode than in the static mode.

It should be noted that the pH of ground water in tuffaceous rocks at the Nevada Test Site has a range from 6.8 to 8.9 (USGS Technical Letter 474-158, Jan. 1973).

FIG. 4

FIG. 5A

FIG. 5B

EXPLANATION OF RESULTS

GENERAL STATEMENT

The experimental results presented here suggest that the sorptive capacity of rock with respect to a specific cation of interest (in this case, Sr^{++}) is greater in the dynamic mode of testing than in the static mode. This result is contrary to the writer's intuitive prediction of the outcome prior to beginning the experiments. The early prediction was based on the fact that the amount of sorption is a strong function of grain size, i.e., the greater the amount of available rock surface area, the greater the sorptive capacity of the rock. It was expected that the fine-grained rock powder used in the static experiments would, gram for gram, sorb more Sr^{++} than the whole rock core used in the dynamic experiments. The expected results did not occur, indicating that an unforeseen factor overshadowed the surface-area effect. A working hypothesis which explains the empirical data is presented below.

WORKING HYPOTHESIS

All of the solutions from static and dynamic tests with Ttt were analyzed for Na^+ , K^+ , and Ca^{++} . The analytical results for the static experiments are presented in Figs. 6a and 6b. It should be noted that in all sorption experiments, the strontium solutions were made with deionized water and no competing cations were added to the solution. Therefore, the Na^+ , K^+ , and Ca^{++} present in solution are derived from the rock material, ostensibly as a result of dissolution and/or leaching of the fine-grained rock material. The dissolving or leaching of a small amount of rock material during static testing is not unexpected; the process being facilitated by the fact the (1) the rock is in a powdered form and (2) the sample is repeatedly agitated during the experiment.

The cations introduced into the solution by means of dissolution become competitive with Sr^{++} for sorption sites on the rock material. The data in Figs. 6a and b suggests that Na^+ and K^+ are formidable competitors to Sr^{++} but that Ca^{++} is significantly less competitive and is strongly partitioned into the solution phase. The amount of Ca^{++} ion in solution continues to increase with time, i.e., it continues to be introduced into the solution via dissolution and is not appreciably sorbed. One would expect the Na^+ and K^+ curves to be similar in form to the Ca^{++} curve if the pair were not being sorbed by the rock material. Instead, the Na^+ and K^+ curves exhibit a flat-topped character and their concentrations in solution show a decrease after the fifty-hour mark. Note that the Na^+ and K^+ curves in Fig. 6a and b are mirror images of the plot for the Sr^{++} concentration in the solution.

COMPOSITION IN P.P.M.'S OF SOLUTION IN STATIC
EXPERIMENT (pH=7, >14 MESH)

FIG. 6A

A plausible model for the sorption process in the static mode is as follows: (1) Sr^{++} adsorption is prevalent during the very early stages of a static experiment when it is the predominant ion in the solution, and (2) Na^+ and K^+ sorption become prevalent subsequent to the attainment of a certain small threshold concentration of these ions. As equilibrium is approached in the ion exchange process, a small amount of total sorbed Sr^{++} is replaced by Na^+ and K^+ .

It is felt that the flat-topped character of the Sr^{++} , Na^+ and K^+ curves belie the fact that the approach to ion exchange equilibrium in the static experiments is a gradual process rather than an abrupt one. Although difficult to prove analytically, it is suggested that, after the first hour of a static experiment, a steady state is attained in which the number of Na^+ and K^+ ions being added to the solution via dissolution is approximately equivalent to the number of ions being taken up by the rock via sorption. Therefore, it is proposed that the flat-topped Na^+ and K^+ curves do not represent a state of equilibrium, but instead, a process in which the rate of dissolution is approximately equivalent to the rate of sorption. This model is consistent with several experimental observations. First, the basic shape of the Na^+ and K^+ curves are quite different from the Ca^{++} curve in Figs. 6a and b. In the case of pure dissolution (without subsequent sorption) one would expect the curves to have a similar shape, i.e. continually increasing with respect to time. The dissimilarity in shape is attributed to sorption of Na^+ and K^+ subsequent to dissolution. Second, the attainment of equilibrium and/or sorptive capacity in the dynamic experiments is achieved in a very gradual manner, therefore the same might be expected in the static mode. And finally, it is felt on an intuitive basis that the total sorptive capacity of a powdered rock is as large as, if not larger, than a whole rock. In the case of static experiments, it is suggested that one observes some of the sorptive capacity being filled with ions introduced during the experimental process, i.e., Na^+ and K^+ , rather than with the specific ion of interest.

During the course of a dynamic experiment, the amount of dissolution of Na^+ , K^+ and Ca^{++} is, gram for gram, about half the amount observed in the static experiments. More importantly, the newly dissolved cations are continually flushed from the system during the experiment so that, subsequent to the initial samples, their concentration is always lower than that observed in the static experiments. Thus, the process which ostensibly accounts for the reduced sorption of Sr^{++} in static experiments is essentially nonexistent in the dynamic mode (Fig. 7).

COMPOSITION IN P.P.M.'S OF SOLUTION IN STATIC EXPERIMENT (pH=7, < 170 MESH)

FIG. 6B

COMPOSITION IN P.P.M.'S OF FILTRATE IN DYNAMIC EXP. (pH=7, 71.9g CORE)

FIG. 7

SUMMARY AND CONCLUSIONS

A preliminary set of experiments has been conducted in order to determine the sorptive characteristics of rock with respect to ionic species under conditions of dynamic flow of an aqueous solution through a rock core. The results of the dynamic experiments have been compared to the results of static or batch experiments which were conducted under corresponding physical and chemical conditions. It was found that, gram for gram, sorption of the ion of interest was always greater in the dynamic experiments. These results are contrary to early predictions and indicate that the effect of rock surface area on adsorption was overshadowed by another parameter.

It has been suggested as a working hypothesis that the competitive effect of ions that were dissolved and/or leached from the rock in batch experiments has resulted in reduced sorption of the ion of interest. Several experimental observations support this hypothesis. The hypothesis could be further tested by means of the following: (1) analyzing the solution in batch experiments for other components (Si, Al, Mg, Fe) in order to further define the dissolution/leaching process by which Na, K and Ca are introduced into the solution, (2) conduct more sets of corresponding static and dynamic runs in order to obtain a larger sampling of results and (3) conduct static and dynamic runs on rock types with a variety of mineralogical make-up.

If the hypothesis is confirmed by further experimental work, a ramification of the study is that calculations concerning transport of radioactivity in groundwater which utilize input parameters derived from static tests will tend to be conservative with respect to what occurs in nature.

SUGGESTIONS FOR FUTURE WORK

The experiments conducted in this study represent a relatively simple mode of testing in that (1) the rock material used in the dynamic and static runs was not pre-equilibrated with an aqueous solution prior to introducing the Sr^{++} solution and (2) no competing cations were added to the solutions. Subsequent to defining the mechanism which accounts for the enhancement of sorption under dynamic flow conditions, the experimental technique can be modified by incorporating pre-equilibration procedures and introducing competing cations. Each of these procedures would bring the experiments a step closer to natural conditions.

The sorptive capacity was the parameter measured in the present study but it should be noted that the distribution coefficient (K_D) is the required input parameter in solute transport calculations. The K_D is commonly defined as

$$K_D = \frac{A_s V_w}{A_w V_s}, \quad \text{where}$$

A_s = fraction of cation in solid

A_w = fraction of cation in solution

V_w = volume of solution

V_s = volume of solid.

In future work, the K_D determined in batch experiments as a function of various competing cations would be compared to the K_D measured in the dynamic mode by means of column elution techniques (Mayer and Thompkins, 1947, J. Amer. Chem. Soc. 69 p. 2866-74).

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