

MASTER

RADIONUCLIDE SORPTION

STUDIES ON ABYSSAL RED CLAYS*

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ABSTRACT

The radionuclide sorption properties of a widely distributed abyssal red clay are being experimentally investigated using batch equilibration techniques. This paper summarizes sorption equilibrium data obtained when 0.68 N NaCl solutions containing either Tc, U, Pu, Am or Cm were contacted with samples of the red clay and also summarizes some initial results from experiments designed to determine the relative selectivity of the clay for various nuclides.

Under mildly oxidizing conditions, the sorption equilibrium distribution coefficients for technetium were essentially zero. At solution-phase nuclide concentrations on the order of 10^{-6} M and less and at solution pH values of about 6.9, the distribution coefficients for plutonium were about 3×10^3 ml/gm and for uranium, americium, and curium were about 10^3 ml/gm or greater. However, at solution pH values of about 2.7, the distribution coefficients for each of the nuclides were greatly diminished. Initial experiments conducted in order to determine the relative selectivity of the clay for cesium, barium, and cerium indicated that the silicate phases in the clay were selective for cesium over barium and cerium. These experiments also indicated

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that the hydrous oxide phases were selective for cerium over barium and for barium over cesium.

INTRODUCTION

The equilibria for the sorption of radionuclides by a widely distributed abyssal red clay are being experimentally investigated. An earlier paper¹ summarized a portion of the investigation concerned with sorption of Rb, Cs, Sr, Ba, Ag, Cd, Ce, Pm, Eu and Gd from aqueous 0.68 N NaCl solutions containing a single nuclide of interest. This paper summarizes more recent work concerned with sorption of Tc, U, Pu, Am or Cm from 0.68 N NaCl solutions and with determining the clay's relative sorption selectivities for cesium, barium, and cerium.

EXPERIMENTAL

Acquisition of and chemical and mineralogical analyses of the red clay samples were discussed in the earlier paper and by Heath. The principal results of the analyses were that the clay was dominated by iron-rich smectite and contained lesser, varying amounts of phillipsite and five to six weight percent hydrous iron and manganese oxides. Sorption equilibrium data for Tc, U, Pu, Am, and Cm in 0.68 N NaCl solutions and for determining relative sorption selectivities were obtained using batch equilibration techniques similar to those discussed in the earlier paper. Typical equilibration times were on the order of two to four days.

RESULTS

Summary of Previous Results

The distribution coefficient K_{D_i} for nuclide i is defined by

$$K_{D_i} = \frac{\text{solid-phase equilibrium concentration}}{\text{solution-phase equilibrium concentration}}$$

For the nuclides studied, the distribution coefficients varied nonlinearly from about 10 to 10^7 ml/gm as the solution-phase nuclide concentration varied from about 10^{-2} to 10^{-11} M, respectively. The distribution coefficients were relatively insensitive to pH at values between 6 and 8, but with the exception of cesium were greatly diminished at pH 2.7.

At least two mechanisms appeared to be involved with the sorption

of each nuclide. One mechanism is believed to be an ion-exchange phenomena associated with the silicates and dominates sorption at higher solution-phase concentrations (greater than 10^{-3} M). The second mechanism dominates at lower solution-phase concentrations (less than about 10^{-4} M) and for cesium is apparently associated with the silicates. However, for the other nuclides, except rubidium, the second mechanism is apparently associated with the hydrous metallic oxides.

Results For Technetium in 0.68 N NaCl Solutions

During preparation of samples for the batch equilibration experiments, both solutions and sediment came in contact with atmospheric oxygen. Furthermore, the polyethylene bottles used for sample containers were permeable to oxygen. Therefore, the batch equilibration experiments were essentially done under mildly oxidizing conditions. The technetium isotope used was ^{99}Tc , which was added as the pertechnetate anion at initial technetium concentrations of about 2.5×10^{-5} mg-atom/ml. The resulting distribution coefficients for technetium were essentially zero at solution-phase pH values of both 8.2 and 2.6.

Results For Actinide Elements in 0.68 N NaCl Solutions

Preliminary sorption experiments were conducted using U, Pu, Am, and Cm. For these experiments, the initial oxidation states of the nuclides were not determined. However, as supplied by the manufacturer the oxidation state of the uranium should have been (VI); the oxidation state of the plutonium was probably predominately (IV), and that of americium and curium was probably (III). In particular the solution in the shipping vial for the americium had a distinctly pink color, characteristic of Am(III).

Uranium. Distribution coefficients for uranium in solutions having pH values of 2.8 and 7.1 were determined using an initial solution-phase concentration of about 3.1×10^{-8} mg-atom/ml. The resulting data are shown in Figure 1. The magnitude and the strong pH dependence of the distribution coefficients are similar to those observed with the lanthanides (Fig. 2). Unlike experiments with the lanthanides or with plutonium, americium, and curium, the uranium experiments were apparently not complicated by decreases in solution-phase tracer concentrations in "blank" samples. Furthermore, additional sorption experiments with uranium were conducted using clay from which the hydrous iron and manganese oxides had been leached. The solution-phase pH for these experiments varied from 7.4 to 8.2, and the resulting distribution coefficients were essentially zero. Furthermore, it was found that the uranium could subsequently be quantitatively removed from the solution phase by coprecipitation with $\text{Fe}(\text{OH})_3$. Such results

indicate that the same mechanisms which dominated sorption of the lanthanides also probably dominate sorption of uranium, particularly the mechanisms thought to be associated with the hydrous oxide phases.

Americium and Curium. Distribution coefficients for americium and curium in solutions having pH values of 2.7 and 6.9 were determined using initial solution-phase concentrations of 3.6×10^{-6} and 6.7×10^{-9} mg-atom/ml, respectively. The resulting data are shown in Figure 1 and are compared with similar data for some lanthanide elements in Figure 2. The magnitude and strong pH dependence of the distribution coefficients for americium and curium are similar to those observed for the lanthanides and again appear to indicate that the same mechanisms dominate sorption. (Note: The solution phase concentrations for promethium which were given in the earlier paper were in error; the correct values are given in Figure 2.)

Also as observed with the lanthanides, significant decreases in solution-phase tracer concentrations occurred in "blank" samples. Some typical data have been included on Fig. 1.

The method discussed in the earlier paper was used to calculate distribution coefficients using data from the sorption and "blank" experiments. Since the competing processes are not yet understood, the calculation of sorption distribution coefficients from experimental data involves substantial uncertainties, which in Figures 1 and 2 may account for the scatter in the lanthanide and actinide data for low solution-phase nuclide concentrations and high pH values.

Plutonium. Distribution coefficients for plutonium in solutions having pH values of 2.7 and 6.9 were determined using an initial solution-phase concentration of 6.4×10^{-6} mg-atom/ml. The resulting data are shown in Figure 1. At comparable solution-phase concentrations, the magnitude of the distribution coefficients for plutonium appear somewhat less than for americium, curium, and the lanthanides. Furthermore, the pH dependence of the distribution coefficients for plutonium does not appear to be as pronounced. Significant decreases in solution-phase plutonium concentrations occurred in "blank" samples, and some typical data have been included on Fig. 1. Distribution coefficients for plutonium were calculated in a manner similar to those for americium, curium, and the lanthanides. At higher pH values, decreases in the plutonium concentrations were much less than the decreases observed for the americium and curium "blanks". Assuming the oxidation state of the plutonium was predominantly (IV), then the "blank" samples imply that at pH 8.3 considerably more

plutonium apparently remained in solution than would have been expected based on the solubility product for $\text{Pu}(\text{OH})_4$.³ Therefore, the data for plutonium appears to indicate that the dominant sorption mechanisms are probably the same as for americium, curium, and the lanthanides; however, the competing solution-phase reactions involving plutonium are more complicated.

Relative Sorption Selectivities

As an initial step toward obtaining multicomponent sorption equilibrium data, two-component experiments in which a nuclide of interest is sorbed from a 0.68 N chloride solution of a competing nuclide other than sodium have been conducted. For such experiments, the preference of the clay for species i rather than species j can be represented by the selectivity coefficient K_{ij}^i which is defined by

$$K_{ij}^i = (\bar{C}_i/C_i) / (\bar{C}_j/C_j) = K_{D_i} / K_{D_j}$$

where \bar{C}_i and \bar{C}_j denote, respectively, the concentrations of species i and j associated with the clay phase. The coefficient K_{ij}^i includes selectivity effects resulting from interactions associated with both solution and clay phases.^{4,5} For the experimental conditions used, $K_{D_i} \approx 1$, and $K_{ij}^i \approx K_{D_i}$. If $K_{D_i} > 1$, the clay is selective for species i .

Since at higher solution-phase concentrations, the silicate phases appear to dominate sorption, it was felt that values of K_{ij}^i corresponding to nuclide concentrations greater than 10^{-3} M would reflect relative selectivities associated with the silicates. Similarly, it was felt that values of K_{ij}^i corresponding to solution-phase concentrations on the order of 10^{-6} M and less would reflect selectivities associated with the hydrous oxides.

The two-component batch equilibration experiments were conducted at 4°C and atmospheric pressure and involved the following pairs of nuclides: cesium and barium, cesium and cerium, and barium and cerium.

Values of K_{ij}^i were determined for each nuclide at two different concentrations in 0.68 N chloride solutions of the competing nuclide. The higher of the two concentrations was about 10^{-3} M and the lower was on the order of 10^{-6} M or less. Solution pH values for the various pairs of nuclides ranged between 5.2 and 7.2.

From the experimental data,⁶ relative sorption selectivities associated with both silicate and hydrous metallic oxide phases were determined. The silicate phases appear to be selective for cesium over barium and cerium; however, the precision in the experimental data is insufficient to resolve the

selectivity of the silicates for barium relative to cerium.⁷ Analysis of data from the previously reported experiments indicated that the silicates should probably be selective for barium over cerium.⁴ The hydrous metallic oxide phases appeared to be selective for cerium over barium and for barium over cesium.

CONCLUSIONS

The same mechanisms which dominate sorption of the lanthanides also apparently dominate sorption of the actinides. However, in the case of plutonium the effects of competing solution-phase reactions are more pronounced.

The relative sorption selectivities determined from the two-component experiments with cesium, barium, and cerium generally appear consistent with results anticipated from earlier experiments involving cesium, barium, or cerium in 0.68 N NaCl solutions. However, more refined and precise experiments are required in order to definitely resolve selectivities between cerium and barium in the silicate phases.

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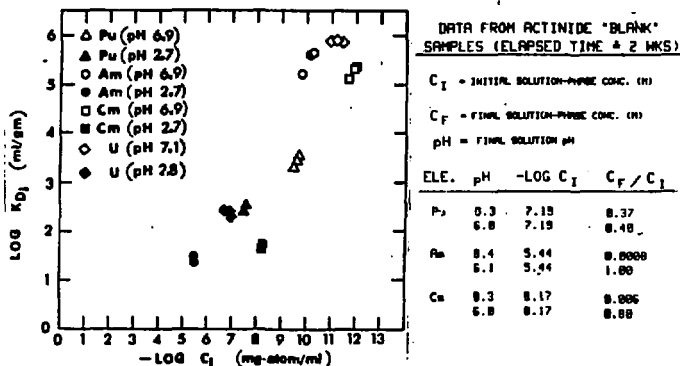


Figure 1. Distribution Coefficients for U, Pu, Am and Cm in 0.68 N NaCl Solutions and Data from Actinide "Blank" Samples.

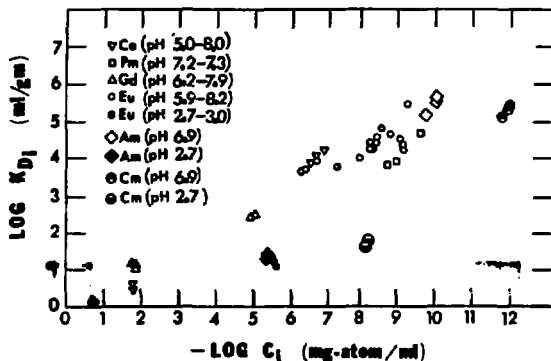


Figure 2. Distribution Coefficients for Ce, Pm, Gd, Eu, Am and Cm in 0.68 N NaCl Solutions.