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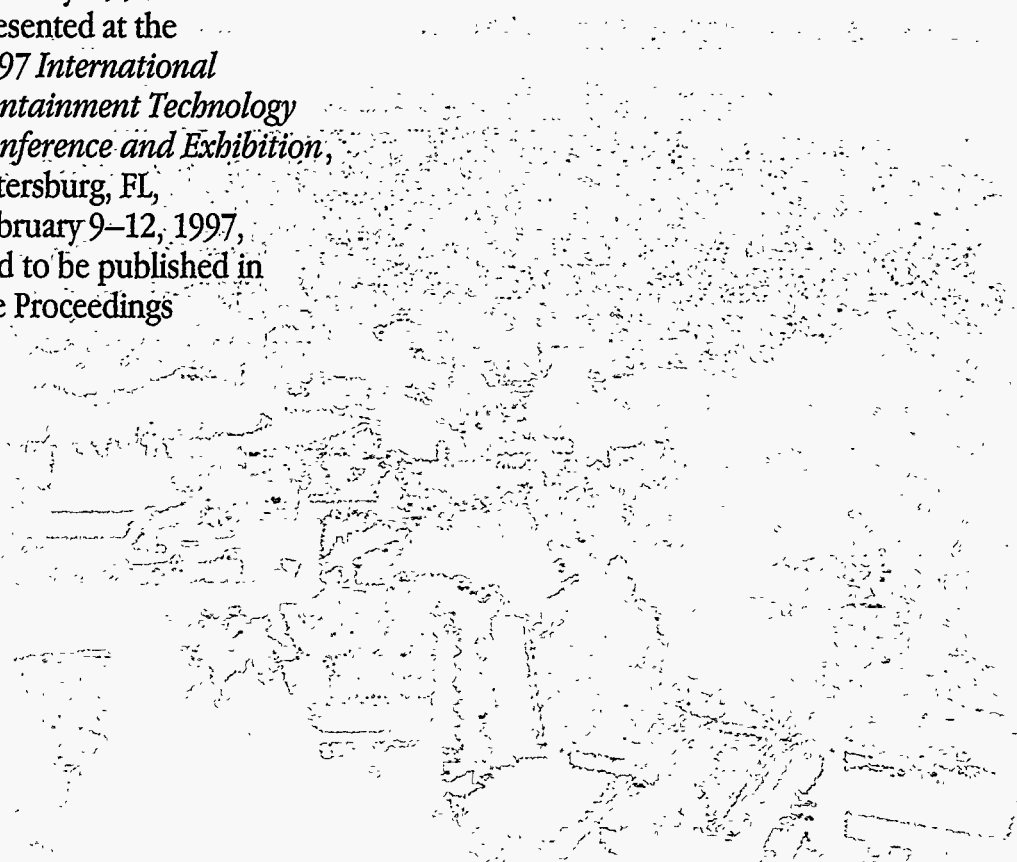
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January 1997

MASTER

Sorption of Cesium and Strontium on Savannah River Soils impregnated with Colloidal Silica

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Abstract

The sorption behavior of cesium and strontium on Savannah River Site Soils impregnated with Colloidal Silica was studied using a batch experimental method. The samples were prepared by addition of CS and an aqueous solution of $CaCl_2$ to the soil materials. Sorption studies were conducted after the gelation of the CS samples had occurred. The variation of the sorption ratio, R, as a function of cesium or strontium concentration was examined. The Freundlich isotherm was used to fit the data and very good results were obtained.

Introduction

Colloidal silica (CS) is being considered as an injectable low viscosity fluid for creation of impermeable barrier containment of low level radioactive waste at the Savannah River Site (SRS), South Carolina.

To determine the effectiveness of the barrier, it is desirable to predict the transport behavior of radionuclides through the barrier. This transport can be modified by several mechanisms such: co- precipitation, adsorption or diffusion (Adeleye *et al.* 1994). If precipitation or strong adsorption occurs, radio-contaminants will be immobilized and the CS barrier will retard radionuclide migration. If the radionuclides diffuse through the CS barrier, the barrier will be less effective in preventing groundwaters contamination (Persoff *et al.* 1994).

The purpose of this work is to study the sorption of cesium and strontium on the colloidal silica and soil from SRS. ^{137}Cs and ^{90}Sr ions, respectivelly, are present in the radioactive waste and potentially mobile as dissolved species under the conditions prevailing at the SRS.

The sorption experiments were performed using a batch method, at different concentrations of radionuclides and at pH constant . The sorption is measured by gamma counting for cesium, by Inductively Couple Plasma (ICP), and by liquid scintillation counting (LSC) for strontium.

Experimental

Reagents

Reagents used in the experiments were: CsCl, ultra pure reagent, $CaCl_2.\ 2\ H_2O$ 99 % pure and $SrCl_2.\ 6H_2O$ 99.8 % pure (J.T. Baker Inc., Phillipsburg, NJ). The isotopes ^{137}Cs and ^{90}Sr (Isotopes Products Laboratories, Burbank, CA) were received respectively as CsCl and $SrCl_2$ in 0.1 M HCl. An Ecolite cocktail liquid (ICN Biomedicals, Inc Irvine, CA) was used as scintillation solution for the radioactive counting. We used Nyacol DP5110 Colloidal Silica (PQ Corporation, Ashland, MA) with the characteristics described in Table 1.

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Table 1. Characteristics of Colloidal Silica Used in our Experiments

Density (g/mL)	1.20
SiO_2	30 %
Na_2O	< 0.1 %
Al_2O_3	< 0.25 %
pH	6.5
Surface specific area (m^2/g)	220
Sites SiO_2 /nm^2	8
Sites Al_2O_3 /nm^2	< 0.5
Particle Diameter (nm)	14

All solutions were prepared with freshly deionized distilled CO_2-free water, even if we don't suspect any presence of carbonates, and were stored under argon atmosphere.

Apparatus and methods

The concentration of ^{137}Cs was measured using the 661.7 KeV gamma-ray of ^{137}Ba and the concentration of ^{90}Sr was measured by liquid scintillation counting. We used a high purity germanium (HPGe) detector designed at LBNL and a liquid scintillation counter, RackBeta, from Pharmacia Inc, Finland.

The pH measurements were performed using a semimicro Ross combination pH electrode calibrated with NIST-traceable standard buffers solutions. The reference solution was 3 M KCl. All experiments were performed at ambient temperature ($23 \pm 1°$ C). The experiments using radiotracers were conducted in an argon atmosphere glove box. Polyethylene vials were used to contain the samples and were kept on a low speed shaking table during the experiment.

Samples were collected from each vial and filtered through 4.1 nm Centricon-30 filters (Amicon Corporation, Beverly, MA). Filters were pre-saturated with the same solutions.

Sample preparation

We carried out three series of experiments using cesium with ^{137}Cs as radiotracer, three series with strontium and three series using strontium with ^{90}Sr as radiotracer. For the cesium sorption study, the initial concentration of CsCl was varied from 10^{-3} to 10^{-8} M. We added 3.0×10^{-9} M of the radioactive isotope ^{137}Cs to each solution in order to use a γ analysis technique that provides a lower detection limit than chemical methods. For the strontium study, the initial concentration of $SrCl_2 \cdot 6H_2O$ was varied from 10^{-2} to 10^{-7} M, ICP being used to determine the concentration of strontium in the solution. For the system with ^{90}Sr, the concentration of strontium as $SrCl_2 \cdot 6H_2O$ was varied from 10^{-4} to 10^{-8} M , we also added 10^{-9} M of ^{90}Sr to each solution to obtain a better detection limit using the liquid scintillation counter. A fourth series with vials containing only Cs or Sr solutions with the different concentrations mentioned above have used as blank samples to correct for any sorption on the walls of the vials. The sorption study of cesium was carried out over a period of 97 days. Table 2 describes the material present in each experimental vial.

Table 2. Description of materials present in experimental vials

Series #	Material	weight of soil (g)	Volume of Colloids (ml)	Volume of 0.3 M $CaCl_2$ (ml)
1	Soil, 5-10 ft depth	15	4.5	0.9
2	Soil , 10-20 ft depth	15	4.5	0.9
3	DP5110	0	4.5	0.9
4	Blank	0	0	0

For each vial of each series we added 30 mL of the corresponding cesium or strontium solution. The mixtures of series 1, 2, and 3 were prepared two days before the addition of any solutions to allow for the colloidal silica gelling process to occur.

The soil consists mainly of quartz(60%) and clay (28%), with minor prsence of geothite (6%) and hematite (6%). The clay mineral in the <2 mm size fraction is primarily kaolinite (99%) with a very minor amount of vermiculite (1%). The soils were dried in an oven for 16 h at 100° C before addition of colloidal silica and calcium chloride.

Results and Discussion

To evaluate the sorption of each element, we used the sorption ratio coefficient which is defined as: $R = \dfrac{C_0 - C_f}{C_0}$ where :

C_0 = initial concentration of the element of concern (Sr or Cs) (M)

C_f = final concentration of the element of concern (Sr or Cs) (M)

a) Cesium Sorption

For cesium, the sorption is significant for all systems as R is generally higher than 0.9 and occasionally reached a value of 1. As can be seen in figure 1, the curve is almost flat in the range from 10^{-6} to 10^{-8} M. This part of the curve represents the maximum uptake and is considered as the fixation capacity of the materials studied. At higher concentrations of cesium (10^{-5} to 10^{-3} M) the sorption decreases due to incomplete saturation of the free sites on the substrate by cesium ions (Hakem *et al.* 1995).

Figure 2 shows clearly that the sorption is very fast and occured within the few fisrt days. A complete sorption equilibrium was established in 8 days for all series.

b) Strontium Sorption

The sorption data obtained by ICP showed that the presence of calcium, silica, and alumina in the samples interfered with the strontium measurement leading to higher values of Sr concentrations. In addition, the detection limit of the ICP is about 1.25×10^{-6} M, which is higher than some of our experimental concentrations. Figure 3 shows a general tendancy of decrease in sorption as a function of Sr concentration, however, the errors in the measurements are high. We are repeating this study with ^{90}Sr. The presence of ^{90}Sr allows us to achieve a detection limit less than 10^{-9} M with the liquid scintillation counter. This work still in progress.

Data Analysis

We used the Freundlich isotherm to interpret the experimental results. This isotherm is described by the equation : $Q_{ads} = k \; C_{eq}^{n}$ (Sposito 1989)

Q_{ads} and C_{eq} are the concentrations of the nuclide in the solid and liquid phases respectively after the sorption.

n and k are positive values determined by plotting log Q_{ads} against log C_{eq}. Logk and n are the y intercept and the slope, respectively, of the resulting straight line.

The curves obtained for cesium and strontium are plotted in figures 4 and 5, respectively. We obtained straight lines for all experimental systems indicating that the Freundlich isotherm fits our data very well. In table 3, we report the values of n and k for each element. We obtained values

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of n between 0 and 1 which suggest that the structure of the adsorbant surface is heterogenous with an exponential energy distribution of the adsorption sites (Sposito 1989).

Table 3. Values of n and k for cesium and strontium

	Cesium		Strontium	
System	$n \pm 0.05$	$\log K \pm 0.1$	$n \pm 0.05$	$\log K \pm 0.1$
Soil, 5-10 ft depth	0.700	-2.90	0.970	-2.99
Soil10-20 ft depth	0.810	-2.60	0.930	-3.21
CS	0.820	-2.40	1.190	-2.39

Conclusion

The high sorption ratio, R, for both of cesium and strontium suggests that they can be immobilized in the soil at SRS.

Generally cesium sorption is higher than that of strontium because cesium ions have a lower hydration energy which enables the cations to shed their hydration shell upon entering the clay interlayers (28% of soil composition) (Cornell, R.M. 1992).

The sorption behavior on geological material is highly specific and each measured sorption is valid only for specific conditions including pH, concentration of the element considered, presence and concentration of competing ions, temperature, time for equilibrium and method of separation of solid and liquid phases. Therefore all realistic conditions prevailing at the site of interest must be taken into account.

For a better understanding of the role of CS as gel liquid barrier, both desorption and diffusion studies must be done on such material.

Acknowledgement

References

Adeleye, S.A, P.G. Clay and M. O. A. Oladipo. (1994) Sorption of caesium, strontium and europium ions on clay mineral. *J. of Materials Science* ., 29, 954-958.

Cornell, R.M. (199 Adsorption of cesium on mineral: a reveiw. *j.of Radioanalytical and Nuclear Chemistry*, 2) *Articles.*, 171(2), 483-500.

Hakem, N, B. Fourest, and R. Guillaumont. (1995) Sorption of radionuclides at tracer level on mineral colloids. *Sixth Annual International Conference on High level Radioactive Waste Management.*, 237-239.

Persoff, P, G.J. Moridis, J. Apps, K. Pruess, and S.J. Muller. (1994) Designing injectable colloidal silica barriers for waste isolation at the Hanford Site, *Thirty-third Hanford Symposium on Health and the Environmant.*, 87-100.

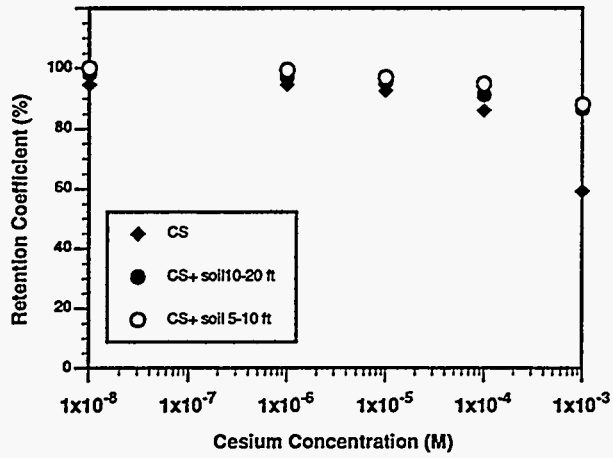Sposito, G. (1989) *The chemistry of soils*, pp.153-154. Oxford University Press.

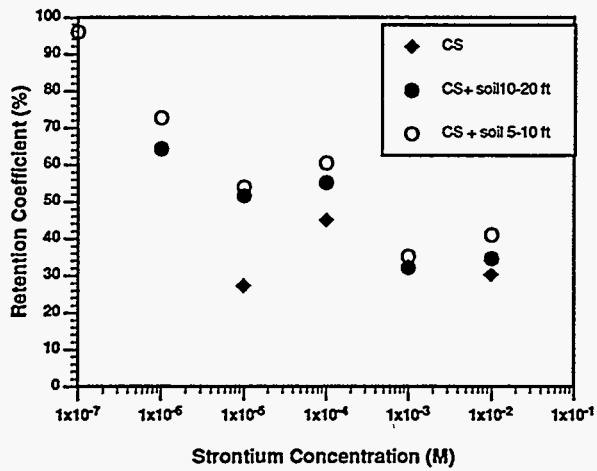**Figure 1. Sorption of Cesium as a Function of its Concentration**

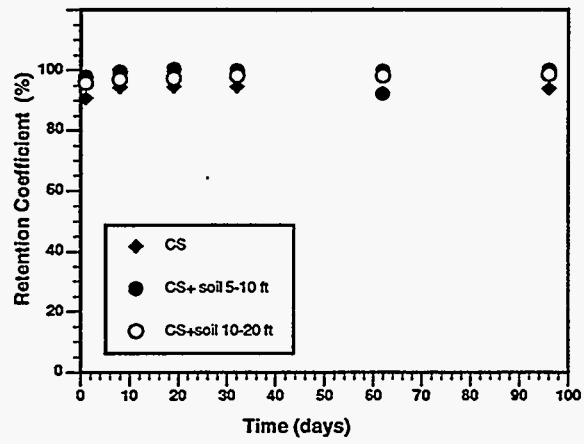**Figure 3. Sorption of Strontium as a Function of its Concentration**

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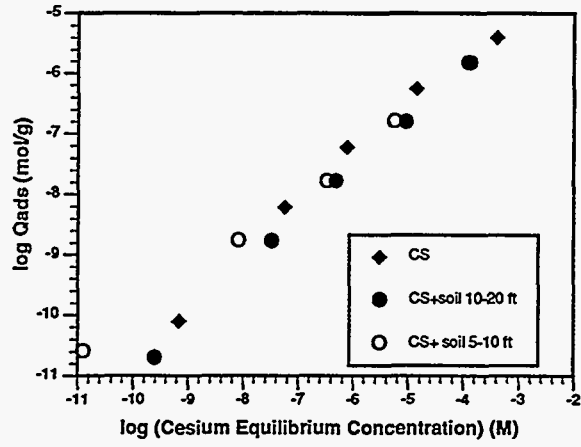**Figure 2. Sorption of Cesium at 1 E-6 M as a Function of Time**

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Figure 4. Variation of the Amount Adsorbed as a Function
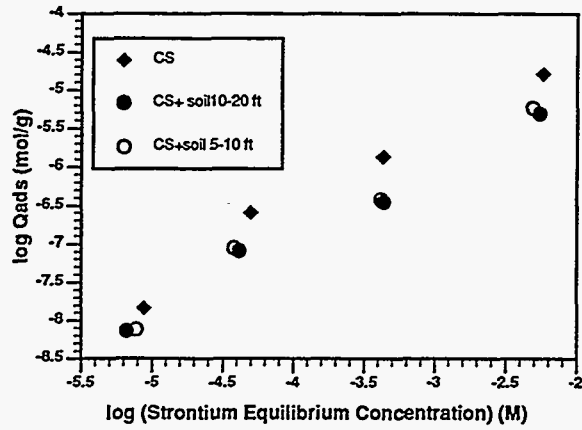of Cesium's Equilibrium Concentration

Figure 5. Variation of the Amount Adsorbed as a Function
of Strontium Equilibrium Concentration

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