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Experimental adsorption studies on different materials selected for developing a permeable reactive barrier for radiocesium retention

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ABSTRACT

Cs-137 was accidentally spilled in an industrial waste repository located in a salt marsh in southern Spain, and a permeable reactive barrier was proposed to retain it. Cs adsorption properties of different natural clayey materials were analyzed. The salt marsh waters show high salinity and high chemical variability, therefore Cs adsorption was also analyzed in the presence of competitive ions, especially K^+ and NH_4^+.

Cs adsorption was non-linear in all the analyzed materials, indicating more than one adsorption sites with different selectivity. It was shown that in mixed clay systems with illite, montmorillonite and kaolinite, the presence of illite favors Cs retention at low and medium Cs loadings and montmorillonite at high Cs loadings. In the presence of illite and montmorillonite, kaolinite plays almost no role in Cs retention. The presence of K^+ and NH_4^+ significantly hinders cesium adsorption.

INTRODUCTION

Cs-137 is a major radionuclide in spent nuclear fuel and in the global radioactive waste inventory. It has been accidentally introduced in the environment by nuclear accidents and from nuclear weapons testing. Radiocesium is particularly relevant from an environmental point of view because it exists predominantly as the monovalent highly soluble cation Cs^+. Geochemical barriers can be designed to retard or stop its migration in groundwater from contaminated zones: many solids are still under study for cesium retention [1,2] but the barriers comprised of argillaceous materials, are reported to be the most effective for its retardation [3].

Thus in this work, for the development of geochemical reactive barrier for cesium, different clayey materials were analyzed to measure their sorption capacity and to understand which minerals contribute most to cesium retention. In order to make the barrier permeable (clays usually have very low permeability) the sorbing fraction will be mixed with other materials, for example, wood shavings with a null sorption capability.

Cesium retention occurs in clays mainly by ionic exchange; therefore the salinity of the waters and ion competition are expected to hinder its retention. The Spanish region, where Cs-137 was accidentally spilled, was located in a salt marsh. The salt marsh waters, affected by the tide, show very high salinity and high chemical variability, therefore Cs adsorption was analyzed

under saline condition and in the presence of ions like potassium and ammonium potentially competitive for Cs adsorption [4,5]

EXPERIMENTAL

Sorption on three different clayey materials (Rojo Carboneros (RC), San Juan (SJ) and Canal de Drenaje (CD)) will be analyzed in this study using 2 different natural saline waters and 0.5 M NaCl. Table 1 shows the main mineralogical composition of the three clayey materials. The main clay minerals are illite, kaolinite and montmorillonite, which is present only in SJ. Table 2 shows the main chemical composition of the two natural waters (W-1 and W-2) used in sorption tests.

Table I. Main minerals present in the three materials under study.

	Clay 1 (RC)	Clay2 (SJ)	Clay 3 (CD)
Illite	57	40	38
Kaolinite	1	12	12
Montmorillonite	---	9	---
Quartz	27	18	26
Calcite/Dolomite	8	4	---
Chlinoclore	---	14	14
Other Minor	7	3	10

Table II. Main chemical composition of the two natural waters used for sorption tests

Element	W-1	W-2
F^-	5	33
Cl^-	17250	60004
NO_3^-	58	1295
PO_4^{3-}	2280	6959
NH_4^+	9	n.a
Ca^{2+}	840	1056
Mg^{2+}	950	3481
Na^+	8500	26555
K^+	286	1179
pH	5	5
Cond. (mS/cm)	42	106

The natural waters present high salinity and the main cations are Na, Mg, Ca and K. The ionic strength of W-2 is approximately 2 times higher than that of W-1.

All the experiments were performed at a room temperature (22-25 °C) and under oxic conditions. The radionuclide used in this study was ^{137}Cs and its activity in solution was measured by γ-counting with a NaI detector (Packard, Cobra II).

Batch sorption experiments were carried out with a solid to liquid ratio of 10 g/L. Kinetic experiments (1 to 35 days) were carried out to determine the equilibrium time. K_d measurements were carried out with $[Cs] = 3 \cdot 10^{-9}$ M and sorption isotherms were carried out by varying the radionuclide concentration from $[Cs] = 1 \cdot 10^{-10}$ M to $[Cs] = 1 \cdot 10^{-3}$ M and a contact time of 14 days. For the experiment with high Cs concentrations (higher than $1 \cdot 10^{-6}$ M), a non-radioactive chemical of high purity (CsCl, Merck) was used in addition to the radiotracer. The solid and liquid phases were separated by centrifuging (22500g, 20 min).

The distribution coefficient, K_d (mL·g-1), is calculated by:

$$K_d = \frac{C_{in} - C_{fin}}{C_{fin}} \cdot \frac{V}{m} \qquad (1)$$

C_{in} and C_{fin} are the initial and final concentration of cesium in the liquid phase ($Bq \cdot mL^{-1}$), m the mass of the clay (g) and V the volume of the liquid (mL). Sorption onto vessels was always lower than <2 %, therefore it was not accounted for K_d calculations.

RESULTS AND DISCUSSION

Figure 1 shows the results of the kinetic sorption experiments carried out with the three clays (RC, SJ and CD) in the two natural waters. The sorption equilibrium is reached around two weeks of contact time in all the cases. At the equilibrium the distribution coefficients range between 80 and 180 mL/g in W-2 and between 480 and 650 mL/g in W-1. The material presenting the lower adsorption capacity was RC, the other two showed similar K_d values.

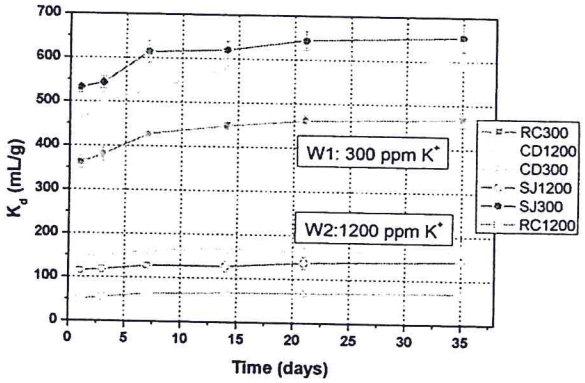

Figure 1. Cesium adsorption kinetic in three different clays (RC, SJ and CD) and two different natural waters (W-1 and W-2).

The chemical composition of the water has then an effect of almost one order of magnitude on the retention capability of the material. Cesium in fact adsorbs mainly by ionic exchange, therefore the higher the salinity the lower the adsorption, as shown in our results. However it is quite important to understand which ions can compete more effectively with cesium for sorption. One of the main difference between the waters that can be mainly responsible for the different sorption behavior is the potassium content: in fact, W-2 has a significantly higher potassium content (about 1200 ppm) than W-1 (about 300 ppm).

Potassium and ammonium are known to be ions especially important in cesium adsorption, because of the existence of sorption sites, related to the presence of micaceous minerals, such as illite, which dominate cesium sorption. For this reason the effect of their presence was especially evaluated and quantified in this study. Thus, the possible effects of the mineralogy of the sorbents, cesium concentration and potassium and ammonium as competitive ions were analyzed more in depth using the SJ and RC clays, simulating saline conditions with 0.5 M NaCl and performing sorption isotherms.

Figure 2 (left) shows the comparison of the sorption isotherms for the SJ and RC clays in NaCl. In both materials, K_d varies with cesium concentration, i.e. cesium adsorption is not linear. This behavior is very typical for cesium above all in the presence of micaceous minerals. Illite, in addition to planar sites, possess frayed edge sites, FES, arising from the weathering of the clay particle's edges, and especially important for alkaline cations adsorption. These sites have very small density (<1% of the CEC of the clay) but adsorb these cations selectively. Cations including Cs^+, Rb^+, Li^+ , NH_4^+, characterized by low hydration energy and small dehydrated radius, can replace K^+ at these weathered edges. Other monovalent ions, such as Na^+, can access these sites only when their concentration is high enough. Yet at these sites, divalent cations with larger sizes and high hydration energy are improbably found.

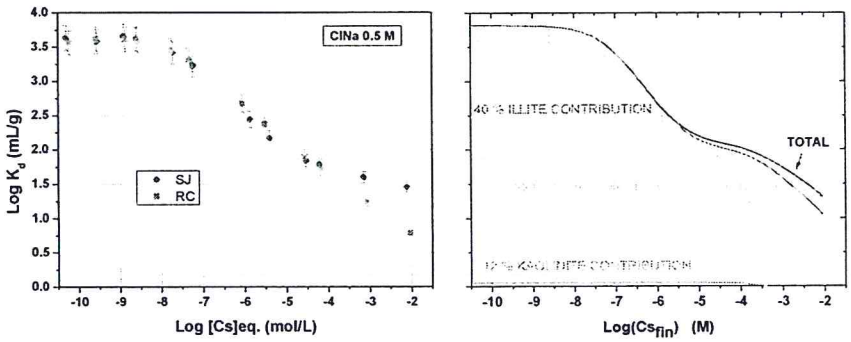

Figure 2. Left: sorption isotherms of cesium onto SJ and RC clays in 0.5 M NaCl. Right: simulation of cesium sorption isotherm in a mixed clay system with 40% illite, 9% smectite and 12 % kaolinite in 0.5 M NaCl. The simulation obtained with the parameters of Missana et al. (2013) is superimposed to the experimental points obtained for the SJ clay, for comparison.

Thus, cesium concentration is a very important parameter in sorption experiments as the variation in K_d values can be more than two orders of magnitude, depending on the selected concentration. K_d values are quite similar in both clays, except for very high Cs concentrations. At these high Cs concentrations, K_d values for SJ are slightly higher than those for RC. This can be due to the presence of montmorillonite in the SJ clay.

To evaluate the presence of potassium and ammonium in the system, sorption isotherms were carried out in both the clays, with 0.5 M NaCl and 782 ppm of K^+ and 360 ppm of NH_4^+ (the molar concentration of both is 0.02 M) as shown in Figure 3. The concentration represents the average value in the contaminated area. Figure 3 (left) shows the results obtained with clay RC and Figure 3 (right) the results obtained with clay SJ.

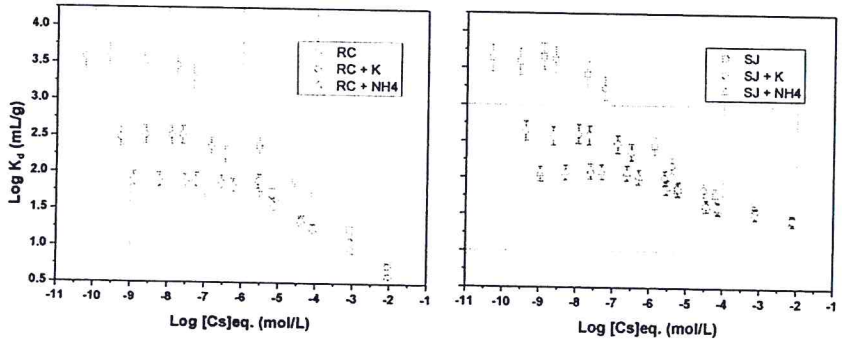

Figure 3. Sorption isotherms of cesium in 0.5 M NaCl and with the additions of K^+ (782 ppm) and NH_4^+ (360 ppm). Left: RC clay and Right: SJ clay.

The effects of potassium and ammonium are evident and similar in both clays, above at low-medium cesium loading, where adsorption occurs mainly in the FES sites of illite. Here, the decrease in K_d values is one order of magnitude or more. Ammonium is more selectively adsorbed than potassium in FES, in fact its presence hinders more effectively cesium adsorption.

CONCLUSIONS

Cesium adsorption has been analyzed onto different clayey rocks under very saline conditions typical of a marsh zone.

The effects of the mineralogy of the sorbent, chemistry of the water and cesium concentration have been evaluated. In particular, the competitive effects of potassium and ammonium (even in such saline waters) have been assessed.

Cesium sorption in all the materials was non-linear, due to the presence of illite, providing highly selective sites for cesium adsorption. Cesium sorption is always dominated by illite at low and

medium Cs loadings whereas montmorillonite starts to be relevant at high Cs concentration. The contribution of kaolinite in the presence of illite and montmorillonite is almost irrelevant

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