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Reactive Barriers for ^{137}Cs Retention

James L. Krumhansl, Patrick V. Brady, Howard L. Anderson
Geochemistry Department (MS-0750)
Sandia National Laboratories, Albuquerque, New Mexico, 87185-0759

Abstract

^{137}Cs was dispersed globally by cold war activities and, more recently, by the Chernobyl accident. Engineered extraction of ^{137}Cs from soils and groundwaters is exceedingly difficult. Because the half life of ^{137}Cs is only 30.2 years, remediation might be more effective (and less costly) if ^{137}Cs bioavailability could be demonstrably limited for even a few decades by use of a reactive barrier. Essentially permanent isolation must be demonstrated in those few settings where high nuclear level wastes contaminated the environment with ^{135}Cs (half life 2.3×10^6 years) in addition to ^{137}Cs. Clays are potentially a low-cost barrier to Cs movement, though their long-term effectiveness remains untested. To identify optimal clays for Cs retention Cs desorption was measured for five common clays: Wyoming Montmorillonite (SWy-1), Georgia Kaolinites (KGa-1 and KGa-2), Fithian Illite (F-Ill), and K-Metabentonite (K-Mbt). Exchange sites were pre-saturated with 0.16 M CsCl for 14 days and readily exchangeable Cs was removed by a series of $LiNO_3$ and LiCl washes. Washed clay were then placed into dialysis bags and the Cs release to the deionized water outside the bags measured. Release rates from 75 to 139 days for SWy-1, K-Mbt and F- Ill were similar; 0.017 to 0.021 % sorbed Cs released per day. Both kaolinites released Cs more rapidly (0.12 to 0.05 per cent of the sorbed Cs per day). In a second set of experiments, clays were doped for 110 days and subjected to an extreme and prolonged rinsing process. All the clays exhibited some capacity for irreversible Cs uptake so most soils have some limited to act as a natural barrier to Cs migration. However, the residual loading was greatest on K- Mbt (~0.33 wt% Cs) . Thus, this clay would be the optimal material for constructing artifical reactive barriers.

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Introduction

^{137}Cs has been introduced to soils and groundwater over the past five decades by nuclear accidents, as fallout from nuclear testing, and as a byproduct of nuclear research and weapons production. Although its half-life is relatively short (30.2 years) it emits both intense gamma and beta radiation. This radiation, and its chemical similarity to potassium - a nutrient, makes transport of ^{137}Cs in the biosphere a pressing concern. Additional concern arises from long lived ^{135}Cs (half life 2.3×10^6 years) that may be masked initially by the more active ^{137}Cs, but may present a longer term isolation problem at a few sites where significant amounts of high level nuclear wastes have leaked into the environment. Because of their dispersed nature Cs contamination plumes can be difficult (if not impossible) to remove. As a result, reactive barriers are becoming an increasingly attractive alternative for containing the radioactive Cs contamination until radioactive decay reduces the radiation to innocuous levels (typically about 10 half lives of the isotope of concern). Various clays would seem to present the greatest possibility of achieving this goal at minimal cost.

Although Cs does not form insoluble compounds under normal aquifer conditions, the literature contains numerous references to the binding of Cs by clays, particularly illite (Tamura, 1972). Ion exchange for alkali metals is clearly at the core of the process, yet the interaction is complex and apparently not completely reversible. In fact, Cs ions initially sorbed onto illite by normal ion exchange processes apparently migrate to interlayer sites exposed along the edges of the clay platelets -"frayed edge sites" (Evans, et al, 1983; Jacobs and Tamura, 1960). The Cs then loses its hydration waters and the bare ion moves into the hexagonal indentations on the face of the layer. This repairs a local charge defect allowing adjacent layers to come together in the manner of a normal clay lattice. This isolates the Cs from the surrounding solution and it is only released very slowly, if at all. Cs sequestered in this manner may remain isolated long enough that radioactive decay would preclude it reentering the biosphere.

Although the literature of Cs uptake by clays and soils is extensive, relatively few studies address Cs desorption:

1. Komarneni (1978) found that Cs retained on kaolinites after being rinsed in 0.02 N sodium or calcium chloride solutions correlated well with the impurity level in the clay (persumably micaceous or illitic components). A completely pure kaolinite released all of its Cs after three rinses.

2. Coleman and Le Roux (1965) investigated the release of Cs from previously loaded vermiculite-rich soil. Ion exchange was the dominant mechanism of Cs release, yet the release of Cs from interlayer positions was much slower than normal ion exchange processes. Cs releases from the montmorillonite fraction of the soil were rapid and complete. This differs from Ohnuki and Kozai (1994), who found that their smectite did, in fact, "irreversibly" sorb Cs.

Comans and Hockley (1992) described Cs sorption on illite with a "two box" model. Cs-containing solutions are envisioned to equilibrate with an instantaneously reversible site. Cs-loading is proportional to the dissolved Cs concentration. Reversibly sorbed Cs can then exchange with a "fixed" site, the transfer of Cs between reversible and fixed sites being governed by two kinetic parameters describing fluxes in the forward and reverse directions. The "half -life" for the loading of the "fixed site is roughly 50 - 125 days. The reverse reaction (desorption) has a " half life" of about 10 years (Smith and Comans, 1996).

Unfortunately, the literature does not contain comparative stuides regarding the relative ability of different clays to retain Cs over long time spans. The exchange capacity of kaolinite is know to be low with respect to smectites and illites , but kaolinite is of interest because important nuclear sites (e.g. the Savannah River Reservation) are located on kaolinite-rich soils. In addition, the amounts of Cs to be sequestered are typically small (a few grams, or under extreme conditions of leaked high level nuclear waste, kilograms). Thus, with a barrier containing many tons of clay the loading capacity is less of a concern than the ability of the clay to retain Cs once it has been sorbed.

Experimental Methods

Although the broad outlines of Cs uptake by clays are fairly straight-forward, Cs sequestration has rarely been studied over long periods of time. To remedy this shortcoming five clays were subjected to a variety of tests designed to quantify long term Cs release rates. The five clays included: KGa-1 Georgia Kaolinite - well crystallized clay, TO (tetrahedral + octahedral) lattice type; KGa-2 Georgia Kaolinite - poorly crystallized clay, TO lattice type; SWy-1 Wyoming Bentonite - Na/Ca exchanged initially, TOT (tetrahedral + octahedral + tetrahedral) lattice type; K-Mbt Virginia Metabentonite - K exchanged initially, TOT lattice type; F-Ill "Fithian" Illite, Illinois - K >>Na, Ca exchanged initially, TOT lattice type.

5 g of each clay was treated in 50 ml of 2% CsCl at 25° and 90° C for 14 and 110 days. (The 90° C tests were done to accelerate the overall sorption process rather than to simulate actual aquifer conditions.) The amount of Cs present was sufficient to satisfy all the exchange sites, even those on the SWy-1 bentonite. Fluid from the 14 days samples was analyzed . Na, K, Ca and Mg to determine what ions the Cs displaced.

After treatment, readily exchangeable Cs was removed by rinsing the clays repeatedly with 0.25 M $LiNO_3$, and then LiCl, solutions. Subsequent rinses using deionized water continued until a negative AgCl test was obtained. Washing of the 110 day sample was more aggressive, involving more rinses and up to a week exposure time between rinses. After this extreme rinse cycle the pore fluid dilution factors for the bentonites were roughly 10^{-9}, while for the other clays they were closer to 10^{-11}. All rinses were made with Li salts dissolved in deionized water so the pH should not have deviated significantly from neutrality during the process. Both suites of samples were digested in HF and analyzed for Li and Cs by ICP-MS

A 0.3 g split of each 14-day treated clay was placed in a dialysis bag that was subsequently suspended in 260 ml of deionized water. Fluid samples were repeatedly withdrawn and analyzed for Cs by ICP-MS. The analyst claims reproducibility to within 10% using the technique, but reports results to three places for the higher concentrations. Thus, the three decimal place convention is maintained in the data tabulated here.

Results

The effect of Cs loading procedures on reversible ion exchange sites can be assessed by comparing the cations released (Ca+Na+K+Mg) during the 14 day loading (Table 1a), with the cations loaded onto the Li (Table 1b), and Cs (Table 1c):

1. Heating slightly decreased the exchange capacity (based on the release of Ca+Na+K+Mg) for both kaolinites and Fithian illite. A slight increase was observed for the K-metabentonite and SWy-1 Wyoming bentonite. The comparison of Li levels after 14 days in heated and unheated clays shows similar small differences. However, none of these changes were large enough to indicate that heating (or the other parts of the loading and washing processes) had significantly altered the normal ion exchange properties of the various clays.

2. For both kaolinites (TO – type lattices) the amount of Li loaded onto the clay after the washing greatly exceeded the cations released during the Cs loading step. It is unlikely that either the loading or washing steps degraded the clay or created new exchange sites. The alternative is that the washing displaced some other cation in addition to Ca, Na, K, or Mg The likely explanation is that Li displaced hydrogen ions from the surface hydroxyl sites as well as cations on the normal ion exchange sites (related to the presence impurities with TOT – type lattices in the kaolinite).

3. For the remaining three clays (all TOT- type lattices) the trend is reversed and the exchange capacity based on displaced cations equals (for SWy-1), or exceeds (for F-Ill and K-Mbt) the amount of Cs+Li loaded onto the clay. For Fithinan illite and K-metabentonite the principal displaced cation is Ca. With SWy-1 bentonite, Na and Ca contributed about equally and together account for most of the calculated exchange capacity. Neither the Fithian illite, nor the K-metabentonite are particularly clean clays so some of the disparity in these results may reflect the additional dissolution of trace amounts of calcite.

To summarize, these clays behaved in a manner that was consistent with what would be expected based on the extensive literature regarding normal ion exchange processes in clays. Thus, the sample preparation procedures used for this study did not create clays with unique properties or behaviors that would be non-representative of what could be easily achieved in the field.

Table 1a. Ion Exchange Capacities (meq/100g)[1]

Clay	25°C	90° C
KGa-1	0.54	0.46
KGa-2	0.67	0.58
F-Ill	17.1	17.0
K-Mbt	16.9	17.8
SWy-1	69.7	69.8

[1] Computed from Ca+Na+K+Mg displaced during 14 day Cs loading experiments

Table 1b. Li Content of Clays (meq/100g)

Clay	Untreated	25° C	90° C
14 Days			
KGa-1	0.092	1.20	0.58
KGa-1	0.092	1.20	0.58
KGa-2	1.29	2.65	2.41
F-Ill,	0.354	15.2	11.6
K-Mbt,	0.382	1.12	0.72
SWy-1	0.185	56.6	64.7
110 Days			
KGa-1	0.092	1.19	1.22
KGa-2	1.29	2.81	2.64
F-Ill	0.354	10.3	8.71
K-Mbt	0.382	3.67	4.52
SWy-1	0.185	32.8	34.6

Table 1c. Cs Content of Clays (meq/100g)

Clay	Untreated	25°C	90°C
14 Days			
KGa-1	0.0009	0.034	0.080
KGa-2	0.0004	0. 173	0.210
F-Ill	0.0072	1.76	2.54
K-Mbt	0.0105	4.45	5.05
SWy-1	0.0015	25.5	36.7
110 Days			
KGa-1	0.0009	0.0067	0.010
KGa-2	0.0004	0.0122	0.014
F-Ill	0.0072	0.213	1.47
K-Mbt	0.0105	2.50	3.10
Swy-1	0.0015	0.232	1.00

A key requirement of reactive barriers is the ability to maintain low contaminant release rates, the exact value of which is determined by local hydrologic conditions and the applicable groundwater pollution statutes. Cs release rates were ascertained by putting ~0.3 g of 14 day loaded clays in dialysis bags. These were than placed in 260 ml bottles filled with deionized water and periodically sampled for Cs (Table 2).

Table 2. Cs Release Rates (14 day loaded samples)

Fithian Illite			25°C			90°C
Days	Cs residual*	%Cs lost	$Cs(g)_{lost}/Clay(g)$	Cs residual	%Cs lost	$Cs(g)_{lost}/Clay(g)$
0-5	2.34 ppt	0.038	8.8×10^{-7}	3.36	0.11	3.8×10^{-6}
5-24	2.32 ppt	0.050	1.1×10^{-6}	3.31	0.15	5.1×10^{-6}
24-75	2.23 ppt	0.043	9.9×10^{-7}	3.18	0.10	3.2×10^{-7}
75-139	2.25 ppt	0.021	4.7×10^{-7}	3.03	0.071	2.1×10^{-7}
K-Metabentonite						
0-5	5.41 ppt	3.76	2.0×10^{-4}	6.20	3.29	2.0×10^{-7}
5-24	4.77 ppt	0.28	1.4×10^{-5}	5.43	0.29	1.6×10^{-7}
24-75	4.60 ppt	0.037	1.7×10^{-6}	5.31	0.049	2.6×10^{-7}
75-139	4.52 ppt	0.022	1.0×10^{-6}	5.20	0.028	1.4×10^{-8}
SWy-1 Bentonite						
0-5	33.4 ppt	0.65	2.2×10^{-4}	48.3	0.46	2.2×10^{-4}
5-24	32.4 ppt	0.15	4.9×10^{-5}	47.4	0.059	2.8×10^{-5}
24-75	31.7 ppt	0.025	7.9×10^{-6}	46.9	0.021	1.0×10^{-6}
75-139	31.4 ppt	0.017	5.3×10^{-6}	46.4	0.016	7.3×10^{-6}
KGa-1 Kaolinite						
0-5	45 ppm	0.77	3.5×10^{-7}	182^1	10.6	1.9×10^{-6}
5-24	40 ppm	1.00	4.1×10^{-7}	110^1	2.21	2.4×10^{-6}
24-75	33 ppm	0.47	1.5×10^{-7}	76^1	0.61	4.6×10^{-7}
75-139	28 ppm	0.12	3.3×10^{-8}	70^1	N/A	N/A
KGa-2 Kaolinite						
0-5	228 ppm	0.32	7.3×10^{-7}	277^1	0.20	5.6×10^{-7}
5-24	216 ppm	0.48	1.1×10^{-6}	270^1	0.22	6.0×10^{-7}
24-75	171 ppm	0.33	7.8×10^{-7}	243^1	014	3.5×10^{-7}
75-139	109 ppm	0.046	6.4×10^{-8}	255^1	0.032	7.8×10^{-8}

ppm parts per milllion by weight, ppt parts per thousand by weight

*Cs loading on the clay midway through the respective time interval.

The kaolinites stand out as unsuitable materials for impeding Cs migration because at room temperature both clays lost almost half of their Cs during the relatively short four month study period. This result does not reflect a kinetic problem in accessing strong sites since heating of the kaolinites also failed to fix significant amounts of Cs. KGa-2 is less crystalline than KGa-1 (Van Olphen and Fripiat, 1979), which may account for its lower retention capacity.

The TOT clays are more promising candidates for Cs retention Like kaolinite, an early rapid Cs release occurred but a much smaller fraction of the sorbed Cs was lost. Thus, even after four months of leaching, most of the Cs remained in the TOT clays. Late stage release rates (75 – 139 days) are remarkably similar for all three TOT clays. Movement of Cs into "irreversible" sites was not enhanced by raising the temperature.

Indeed, late stage release rates for both the Fithian illite and K-metabentonite were increased by heating the samples.

Although Table 2 suggests that the fractional Cs releases from TOT – type clays does not depend on mineralogy, this assessment is based on experiments where only a small fraction of the Cs was released. A comparison of the 14 and 110 day loading experiments (Table 1c) suggests that as more Cs is released, mineralogy plays a larger role. The difference in Cs contents between clays subjected to these two treatments is significant in all cases and particularly pronounced for the SWy-1. Essentially all of the Cs was removed from the bentonite by the rigorous washing procedure accorded the 110 day samples. This data supports the findings of Coleman and Le Roux, 1965, and suggests that the bentonite studied by Ohnuki and Kozai, 1994, may have had an illitic component.. The fraction of Cs retained by Fithian illite (and both kaolinites) loaded at room temperature is somewhat higher, but the 110 day sample rinse procedure still removed more than 80% of the Cs found on 14 day treated samples. K-metabentonite is a notable exception. The 110 day samples have fully half the Cs content of the 14 day treated samples. The distinction is even more striking when the absolute concentrations are examined. The Cs content of the 110 day K-metabentonite loaded at room temperature is more than ten times that of the other clays evaluated.

Discussion:

Basis of ^{137}Cs fallout distributions in argillaceous lake bed sediments Smith and Comans (1996) suggested that the release of strongly held Cs has a half life of roughly 10 years. This corresponds to a Cs loss rate of approximately 0.014 % per day, which is in surprisingly good agreement with the late stage rates observed for TOT clays in this study, 0.017 – 0.022 % Cs lost per day. Since widely differing approaches arrived at essentially the same value, it is probably reasonable to use the latter release rates to predict where locally available illitic or montmorillonitic clays might constitute a natural barrier to Cs migration. In these settings a performance calculation employing retention kinetics based on a two box models (Comans and Hockley, 1992) should be useful in discerning whether migrating ^{137}Cs constitutes a health hazard. It is also noteworthy that the kaolinites did not release all of their Cs even after the extreme washing process. Thus, even these clays may have some potential as a natural barrier to Cs migration, though much less than that provided by TOT clays.

In reality, use of the simple two box model would probably provide a conservative overestimate of the extent of Cs migration, as our data indicates Cs sorption/desorption to be more complex than the model implies. Even the more limited washing of the 14 day loaded samples would remove "exchangeable" cations according to standard ion exchange capacity determination procedures (see, for example, Jackson, 1979). This was the justification for comparing the 10 year half life proposed by Smith and Comans (1996) with the late stage release rates from the 14 day samples. In fact, comparison of the 110 and 14 day results suggests that there is more than one kind of "irreversible" site. Consequently, as the Cs in such sites decreases Cs will become progressively harder to remove. Thus, performance assessment calculations that use a 10 year half life will be skewed to using rates at the more rapid end of distribution of possible values.

Finally, it is relevant emphasize where reactive barriers comprised of argillaceous materials are likely to be most effective. To a large degree this depends on the local soil mineralogy but certainly optimal environments include settings where soils are predominately kaolinite or a non-argillaceous sand. In these applications a large degree of latitude is possible regarding the texture of the material incorporated into the barrier. Bentonite is particularly effective as a sealing agent, as well as having a high ion exchange capacity. Alternatively, if a granular non-sealing material is required for a porous barrier (e.g. one that will allow fluid to pass while scavenging radioactive Cs), then crushing shales rich in illite or K-metabentonite should suffice. Swelling associated with the wetting of these materials is small enough that the flow of groundwater will not be blocked. For scoping calculations the late stage solution and solid Cs concentrations from this study can be cast to provide formal Kd values for all three TOT clays: F-Ill = 1.4×10^4 ml/g, K-Mbt = 2.6×10^3 ml/g, SWy-1 = 9.1×10^3 ml/g. However, accurate modeling of barrier performance will eventually require incorporating kinetic aspects of the sorption and release processes.

References:

1. Coleman, N.T., and Le Roux, F.H., 1965, Ion Exchange Displacement of Cesium From Soil Vermiculite) Soil Science, v.99, no. 4, p. 243 - 250.
2. Comans, R.N.J., and Hockley, 1992, Kinetics of Cesium Sorption on Illite, Geochimica Cosmochimica Acta, v. 56, p. 1157 – 1164.
3. Evans, D.W., Alberts, J.J., Clark, R.A. III, 1983, Reversible Ion-Exchange Fixation of Cesium 137 leading to mobilization from reservoir sediments, Geochimica et Cosmochimica Acta, v. 47, p.1041 – 1049.
4. Jacobs, D.G., amd Tamura, T., 1960, The Mechanism of Ion Fixation Using Radioisotope Techniques, 7th Internat. Cong. Soil. Sci.Proc. V.2, p. 206-214.
5. Jackson, M.L., 1979, Soil Chemical Analysis – Advanced Course, 2nd Edition 11th printing, Published by the author, Madison, Wis., 53705), p.252 – 263.
6. Komarneni, S., 1978, Cesium Sorption and Desorption Behavior of Kaolinites, Soil Sci. Soc. Am. J., v. 42. p. 531 – 532.
7. Ohnuki, T., and Kozai, N., 1994, Sorption Characteristics of Radioactive Cesium and Strontium on Smectite, Radiochimica Acta, v. 66/67, p. 327-331.
8. Smith, J.T., and Comans, R.N.J., 1996, Modeling the Diffusive Transport and Remobilization of ^{137}Cs in sediments: The Effects of Sorption Kinetics and Reversibility, Geochimica et Cosmochimica Acta, v. 60, no.6, p. 996-1004.
9. Tamura, T., 1972, Sorption Phenomena Significant in Radioactive Waste Disposal, American Association of Petroleum Geologists Memoir 18, "Underground Waste Management and Environmental Implications, p. 318 – 329. Van Olphen, H., and Fripiat, J.J., 1979, Data Handbook for Clay Materials and other Non-Metallic Minerals, Pergamon press, p. 13-17).