In Situ Remediation of ^{137}Cs Contaminated Wetlands Using Naturally Occurring Minerals

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KEY WORDS: Cesium
Illite
In-situ remediation
Wetlands
Mica

RETENTION: Permanent

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SAVANNAH RIVER SITE

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SAVANNAH RIVER SITE

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EXECUTIVE SUMMARY

Over 1,200 hectares (3,000 acres) of wetlands on the Savannah River Site (SRS) are contaminated with 21 TBq (564 Ci) of ^{137}Cs and pose a significant remediation challenge to the Department of Energy (DOE). These wetlands fall under EPA CERCLA regulations and will be closely scrutinized by SCDHEC, stake-holders and environmental groups. Exposure to ^{137}Cs can pose significant human and ecological risks, and yet remediation of the contaminated wetlands is problematic because current remediation technologies destroy the sensitive ecosystem and generate a higher dose to workers.

The problems of contaminated aquatic systems and their associated risks are heightened on the SRS because ^{137}Cs is more mobile here than at any other DOE facility. Reasons for the high bioavailability of ^{137}Cs are thought to be largely due to the low clay fraction of SRS soils, and that the clay mineralogy is dominated by kaolinites coated with iron oxides. The abundance of the clay fraction is important because ^{137}Cs can be bound within the physical structure of clay minerals (Francis and Brinkley 1976), in essence, trapping ^{137}Cs and reducing its bioavailability. Generally, as the clay fraction increases, bioavailability of ^{137}Cs decreases. However, the mineral structure of kaolinite, a 1:1 clay, does not bind ^{137}Cs as strongly as 2:1 phyllosilicates such as illites and micas.

Each summer, anaerobic processes in the anoxic sediments of thermally stratified lakes on the SRS lead to a release of ^{137}Cs from the sediments. Although representing only a small percentage of the total ^{137}Cs inventory, the amount released is sufficient to cause measurable activity in all components of the wetlands (e.g., water, plants, aquatic insects, fish, etc.), and is the primary driver in human and ecological risks (Whicker, et al. 1993). Because high Cs mobility on the SRS is thought to be due, in part, to poor sorptive properties of SRS kaolinitic-dominated soils, *we tested the hypothesis that an addition of naturally occurring phyllosilicate minerals to wetlands would sequester ^{137}Cs and, thereby, reduce its bioavailability.* In application, the phyllosilicates would be introduced into the wetlands where they would sequester ^{137}Cs in the water column as they settle to the bottom sediments. The phyllosilicates on the bottom sediments would then intercept and sequester ^{137}Cs during its annual summer release from the sediments. If this process works as conceived, the mineral amendments would effectively sequester ^{137}Cs and, thereby significantly reduce its biological uptake.

To ascertain if our concept was fundamentally feasible we designed three experiments to address the following objectives:

- Determine which commercially available clay minerals have high affinities for sorbing ^{137}Cs .
- Determine which of those same clay minerals effectively retain ^{137}Cs in the presence of high concentrations of competing cations (e.g., NH_4^+).
- From the first two experiments, choose clay minerals that are potential amendments and then conduct a proof-of-concept study by testing their ability to reduce ^{137}Cs desorption from contaminated SRS sediments.

Eleven phyllosilicates were evaluated in this study. Among them were five 2:1 phyllosilicates [one muscovite, one biotite (Mica); a montmorillonite (Smectite); and two vermiculites] and one 1:1 clay mineral (Kaolinite). The most important conclusions from the study were:

- Several minerals (IMt-1, IMt-2, Ward's, VId-1) were shown to exhibit strong sorption (high Cs- K_d values) and weak Cs-desorption behavior. Cs- K_d values of $>10,000 \text{ mL g}^{-1}$ and desorption of $<10\%$ (under extremely harsh leaching conditions) were observed for these minerals.
- Specific mineral characteristics beneficial to Cs sorption and retention were identified, and should be used when choosing quarried minerals for this technology. Results suggest that quarried minerals should contain illite (not kaolinite, smectite, or biotite) with moderate levels of K_2O , and should contain low concentrations of surface coatings. Because this study was conducted on reference materials, further work is necessary to confirm these beneficial mineral characteristics in commercial material.
- Incremental additions of two minerals (IMt-1 and VId-1) to Pond B sediments, contaminated over 35 years ago, appreciably intercepted and retained desorbed ^{137}Cs in the presence of high levels of added NH_4^+ . These proof-of-concept data revealed a trend of reduced total activity with increasing amounts of phyllosilicate amendment.

The technology proposed addresses a DOE problem that is intractable without new knowledge. The technique may allow DOE to cleanup ^{137}Cs -contaminated wetlands in an environmentally acceptable manner--thus, winning the support and praise of Federal and State regulators, stakeholders, and citizen action groups. If successful, this *in situ* remediation technique could be a wonderful success story for the DOE, in that, through the use of natural materials, DOE might be able to reduce the bioavailability of a major contaminant in an ecosystem that has been difficult to remediate. We think this has the potential to be an appropriate remediation strategy because it would reduce human and ecological risks, yet have no damaging effects on the wetland.

One intention of this study was to provide information regarding a "go/no go" decision for future work. Since the proof-of-concept was successful and several minerals were identified as potential candidates for this technology, a "go" decision was made. Our results suggest a non-intrusive, *in situ* technology to immobilize ^{137}Cs in sediments may be feasible on the SRS. Future work to take this laboratory proof-of-concept research to the field and to address some applied questions has been proposed.

INTRODUCTION

Cesium Contaminated Wetlands

Numerous aquatic systems on the Savannah River Site (SRS), such as Par Pond and Ponds A, 2, 4, 5 and B, as well as many kilometers of connecting canals, are contaminated with ^{137}Cs , ^{90}Sr and isotopes of Pu. Combined, these reservoirs represent over 1,200 hectares (3,000 acres) of contaminated wetlands. Inventories of ^{137}Cs within these aquatic systems (including site streams) have been estimated at 21 TBq (564 Ci, Carlton et al. 1992). Cesium-137 is often the radionuclide of primary concern in these systems because of its long half-life and biological mobility. Cesium's implication to human health was evident during the draw down of Par Pond. Exposure to ^{137}Cs comprised 95% of the lifetime fatal cancer risks to an adult farmer hypothetically living on the exposed sediments, while ^{90}Sr and Pu's contribution to risks were 0.6 and 4.1%, respectively (Whicker et al. 1993).

All of these aquatic sites fall under EPA CERCLA regulations and thus represent a remediation problem to DOE. Remediation of wetlands is particularly problematic because current cleanup technologies for aquatic system are generally destructive to the ecosystem. If cleanup is required, a likely scenario would entail draining the impoundment and either immobilizing the sediments, where 95% of the radionuclides reside (Whicker et al. 1990), or hauling the sediments off to be buried. These methods would be expensive, would expose workers to inhalation doses, would destroy the associated ecosystems, and would likely invoke negative responses from stake holders, SCDHEC, EPA, and NEPA regulations.

High Cesium Mobility

The problems of contaminated aquatic systems and their associated risks are heightened on the SRS because ^{137}Cs is more mobile here than at any other DOE facility. Increased ^{137}Cs availability was documented in these systems during the 1960s era of weapons fallout (Whicker and Schultz 1982), and the high mobility of ^{137}Cs still exists today, as is evident by the propensity of ^{137}Cs to be taken up by plants. This propensity can be measured using a concentration ratio (CR), where $\text{CR} = \text{Bq kg}^{-1} \text{ dried plant} / \text{Bq kg}^{-1} \text{ dried soil}$. The National Council on Radiological Protection and Measurements recommends a default CR to be used in risk calculations of 0.1. In comparison, CRs for the SRS are generally well above 1.0. Indeed, they are among the highest recorded CRs in the world. Plants from Steel Creek and Par Pond had CRs that ranged from 3 to 7 (Garten and Paine 1977; Pinder et al. 1980), garden vegetables grown on the exposed lake bed of Par Pond had CRs of 6.8 ± 2.3 (Seels et al. 1995), and early successional species invading Par Pond's exposed lake bed had extremely high CRs of 14.9 ± 2.3 (Hinton et al. 1999). Such large CRs indicate the ease with which ^{137}Cs moves in the lower coastal plain, and in part, indicate why ^{137}Cs can be the critical contaminant when human and ecological risk analyses are conducted for the SRS.

Kaolinitic-Dominated Minerals on the SRS

Reasons for the high bioavailability of ^{137}Cs are thought to be largely due to the low clay fraction of SRS soils, and that the clay mineralogy is dominated by kaolinites coated with iron oxides. Sediments of

Par Pond provide a typical example: clay-sized fraction comprised only 1 to 3 % of the textural composition of the sediment (Evans et al. 1983), and 85% of that was kaolinitic (Ruhe and Matney 1980).

The clay fraction is important because ^{137}Cs can be bound within the physical structure of clay minerals (Francis and Brinkley 1976), in essence, trapping ^{137}Cs and reducing its bioavailability. All factors being equal (e.g., clay mineralogy and competing cation (NH_4^+) concentration), as the clay fraction increases, availability of ^{137}Cs generally decreases. The mineral structure of kaolinite (a 1:1 clay), however, does not bind ^{137}Cs as strongly as 2:1 phyllosilicates such as illites and micas. This observation is the basis of our hypothesis that adding phyllosilicate amendments to Cs-contaminated sediments on the SRS may be an effective *in situ* remediation technique.

Mineralogy Overview

Unweathered phyllosilicates like micas can be transformed into illites, vermiculites, smectites, or kaolinites depending on the extent to which they have been physically, chemically, and biologically weathered (reviewed by Fanning et al. 1989). The extent of weathering increases in the order of: mica < illite < vermiculite < smectite < kaolinite (Figure 1). Weathering has a profound effect on a number of physical and chemical properties, which in turn have a direct effect on the mineral's propensity and tenacity to sorb Cs. Selected properties of the minerals used in this study are presented in Table 1 and are described below.

The minerals used in this study can be broadly divided into two classes based on their layer structure. Micas, vermiculites, illites, and smectites have a 2:1 layer structure in which tetrahedral (T) and octahedral (O) sheets are arranged in the sequence T-O-T (reviewed by Bailey 1984 and Fanning et al. 1989). Kaolinite has a 1:1 layer structure arranged in the sequence T-O. The tetrahedral sheets are made up of Si coordinated with four O atoms. The octahedral sheets are made up of either trivalent cations (a dioctahedral 2:1 mineral) or divalent cations (a trioctahedral 2:1 mineral). Minerals with 1:1 layer structures do not contain sites that "irreversibly sorb" Cs.

Mica, illite, vermiculite, and smectite carry net negative charges because not all of the cations in the interstices have sufficient positive charge to balance the charge of the oxygen or hydroxyl anions associated with the mineral structures. For micas and illites, most of the charge is derived from substitution of Al for Si in the tetrahedral sheets. For most smectites, including montmorillonite, most of the charge is derived from substitution of a divalent cation, usually Mg, for a trivalent cation in the octahedral sheets. Kaolinite derives a very small, barely detectable, amount of its charge from isomorphic substitution. Most of the charge of kaolinite particles comes from the edge sites, whose charge increases with pH. The layer charge is highest for young minerals and less for the older minerals.

Figure 1. Diagram illustrating the transformation of a mica (with a nonexpanded interlayer containing potassium) to an illite (with frayed edge sites and expanded layers), and an illite to a vermiculite (with expanded interlayers containing hydrated exchangeable cations) (adapted from Fanning et al. 1989).

The negative charge of the layer is balanced by cations that are located in a plane between the 2:1 layer structures. Although mica and illite crystals carry a large negative layer charge, most of the charge is neutralized by tightly held K ions that are not easily exchanged with other cations. The net negative charge of vermiculites and smectites are balanced with hydrated cations (Figure 1). Due to its low charge, kaolinite particles have relatively few counter ions sorbed to their surfaces and these ions tend to be hydrated divalent cations.

Table 1. Overview of Properties of Selected Classes of Minerals

	Mica	Illite	Vermiculite	Smectite	Kaolinite
Chemical Composition Examples	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ – Muscovite $\text{K}(\text{Mg,Fe})_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ – Biotite	$[\text{MgFeII}]_{0.25}\text{Al}_{1.75}(\text{Al}_{0.5}\text{Si}_{3.5}\text{O}_{10})(\text{OH})_2$	Varied	Varied	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Age	Young	Some substitution of divalent cations for K. Aged from mica.	Often a weathering product from Mica/Illites	Intermediate, often a weathering product from vermiculites	Old. Often a weathering product from smectite or vermiculite
Layer Charge, σ	1.0 moles/formula unit. Lots of substitution in tetrahedral, little substitution in octahedral	0.6 to 0.8 moles/formula unit.	0.5 to 0.9 moles/formula unit	0.6 to 0.25 moles/formula unit. Charge formed by Mg substitution for Al in octahedral sheet (e.g., montmorillonite); Al substitutes for Si in tetrahedral sheet (e.g., nontronite)	Very little, only limited isomorphic substitution and variable charge associated with edge sites: ZPC of edge sites is pH ~7.
Bonding between 2:1 or 1:1 units	Strongest. Because saturated with K^+ , the K^+ has $r = 1.33 \text{ \AA}$, is small enough to fit into ditrigonal hole of tetrahedral sheet	Slightly less than mica	Slightly less than illite	Varies greatly, depends on predominant cation in interlayer, Na^+ weak bond, Al^{3+} strong bond.	Very strong due to H bonding.
X-ray d-spacing for Mg glycerol treatment	1 nm	1 nm	1.4 nm	1.8 nm	0.7 nm
Tactoid Size	Thick, because bonds between tactoids are strong, 5 to 30 nm = 1 tactoid, Often silt size.	Like mica	Smaller tactoid than mica.	Varies, unusually thin, 2 nm for Na saturated, 10 nm if Ca or Al saturated.	Thick and long, 50 nm thick, Kaolinite can be large, silt size.
Specific surface area, a_m	Low. Tactoids are large and little inter-unit area. 70 to 120 m^2/g .	Somewhat larger than mica by virtue of smaller particle size.	Larger than illite	Highest, 100 to 800 m^2/g . Tactoids can be separated in Na saturated minerals	Low because no interlayer, 5 to 20 m^2/g .
CEC	Slightly less than illite	20 to 40 meq/kg	160 meq/kg	80 to 110 meq/kg. High because of high surface area.	Low 0.3 to 1 meq/kg, varies with pH

The size of an individual particle, or tactoid, is a function of a number of mineral properties. Among the most important is the strength of the bond between the 2:1 or 1:1 units. The stronger this bond is, the larger the particle is likely to be. For the 2:1 minerals, mica particles tend to be larger than vermiculites, which in turn are larger than smectites. Kaolinite is commonly a large particle due to hydrogen bonding between 1:1 units. Surface area is inversely related to the tactoid size.

The theoretical cation exchange capacity (CEC) of a mineral is the product of the layer charge and the specific surface area ($\text{m}^2 \text{g}^{-1}$). Vermiculites have the highest CEC, primarily as a result of its high layer charge (Table 1). Smectites also tend to have a high CEC, largely because of their large specific surface area (especially for Na-saturated particles). Micas have a low CEC due to their relatively low surface area (a result of their non-expanding interlayers). Kaolinite has the lowest CEC as a result of low layer charge and surface area. Since kaolinite is the dominant mineral in SRS sediments, little cation adsorption occurs (Carlton et al. 1992).

Fixation of Radionuclides by Micas and Illites

The strong affinity of micas and illites for weakly hydrated, large alkaline cations (K^+ , Cs^+ , and Rb^+) has found its application in radioactive waste disposal. Of these cations, illites and micas sorb Cs^+ the strongest. The reason for this is that the nonhydrated Cs^+ ion fits tightly into the ditrigonal cavities of the tetrahedral sheets (described above). These sorbed Cs^+ ions are preferentially retained in the presence of hydrated cations, such as Ca^{2+} or Mg^{2+} , even though the latter typically occur in concentrations that are 5 to 9 orders-of-magnitude greater in the environment. Because of the high affinity of Cs for micas and illites, it is commonly found fixed in micaceous and illitic soils in a form that is nonexchangeable (Francis and Brinkley, 1976).

All the minerals discussed so far have ditrigonal sites; however, not all of the minerals can "irreversibly sorb" Cs. A number of mineralogical factors are responsible for this (Staunton and Roubaud 1997). One important factor is that the minerals must have a sufficiently high unit layer charge to pull the Cs into the ditrigonal cavity in the tetrahedral sheet while forcing the waters of hydration to remain outside the cavity. All kaolinites and smectites, and most vermiculites lack a sufficient unit charge. The other mineralogical property affecting "irreversible sorption" of Cs, is the number of high-energy ditrigonal sites accessible to the aqueous Cs. Micas have few accessible high-energy sites because of the tight bond between the 2:1 units (Figure 1). Illites, by definition, have frayed-edge sites which expose high-energy sorption sites (Figure 1). It should be kept in mind that in addition to these high-energy sites, both illites and micas have planar sites, which sorb Cs via cation-exchange, and edge-sites which sorb Cs via complexation with surface hydroxides. Kaolinite, vermiculites and smectites only have planar and edge sites.

Studies of Cs adsorption on clay minerals are an interesting example of the strong preference micas exhibit for Cs. Tamura (1972) studied the effect of ionic strength on the preference for Cs of several clay minerals. In the suspensions containing only Cs and no other competing cation, the distribution coefficients (K_d) for Cs were 52,000, 26,000, and 2,500 for $<2\text{-}\mu\text{m}$ vermiculite, illite, and kaolinite, respectively. The

K_d values decreased with decreasing cation exchange capacity of the three minerals (127 cmol kg⁻¹ for vermiculite, 20 cmol kg⁻¹ for illite, and 11 cmol kg⁻¹ for kaolinite). However, when the experiment was performed with 0.1 M NaCl as a background electrolyte, the K_d values were 2,700; 28,600; and 94, respectively. Clearly, Na competed with Cs for the exchange sites on vermiculite and kaolinite, but on illite Cs remained highly preferred. Comparable results were reported by Staunton and Roubaud (1997) in a study of Cs exchange with K, Na, and Ca on illite and montmorillonite.

OBJECTIVES

An inventory of ¹³⁷Cs distribution in Pond B on the SRS revealed that over 95% of all the cesium was associated with the sediments (Whicker et. al. 1990). In summer, lakes on the SRS thermally stratify and the colder, deeper hypolimnion layer becomes anoxic (Figure 2; Hinton, unpublished data). Anaerobic processes in the anoxic sediments produce NH₄, a monovalent cation with a high affinity for displacing ¹³⁷Cs sorbed to mineral surfaces. This processes are thought to increase the bioavailability of ¹³⁷Cs (Figure 3a).

FIGURE 2. Monthly oxygen profiles as a function of depth (m) in Pond 4 on the SRS (Hinton, unpublished data). Low dissolved oxygen concentrations from May to September are thought to contribute to anoxic conditions, a buildup of NH₄ in the sediments from anaerobic processes, and a concomitant release of ¹³⁷Cs from the sediments.

Figure 3a. Annual summer release of ¹³⁷Cs (depicted by solid circles) from anoxic sediments disperses contamination throughout the aquatic ecosystem in the fall and winter. Release of Cs is thought to be coupled to a buildup of NH₄ in anoxic sediments when the lake is stratified.

Because high Cs mobility on the SRS is due, in part, to a low adsorptive capability of kaolinitic-dominated soils, we wanted to test the hypothesis that adding naturally occurring phyllosilicates to wetlands would sequester ¹³⁷Cs and reduce its bioavailability. In application, the naturally occurring phyllosilicates would be introduced into the wetlands where they would sorb ¹³⁷Cs in the water column as they settle to the bottom sediments. The minerals would then intercept and adsorb ¹³⁷Cs during the annual summer release of ¹³⁷Cs from the contaminated sediments, effectively sequestering the contaminant and drastically reducing biological uptake (**Figure 3b**).

To ascertain if our concept was fundamentally feasible we designed three experiments to address the following objectives:

- Determine which commercially available minerals have high affinities for adsorbing ¹³⁷Cs.
- Determine which of those same clay minerals effectively retain ¹³⁷Cs when present among ions that have a high affinity for cesium adsorption sites (i.e. NH₄).
- From the first two experiments, choose minerals that are good candidates as sediment amendments, and then test their ability to reduce the amount of ¹³⁷Cs desorbed from contaminated SRS sediments.

Figure 3b. Addition of clay mineral amendment intercepts released ^{137}Cs and reduces its availability. Added minerals are illitic with a 2:1 structure that characteristically adsorb Cs much better than the kaolinitic-dominated minerals typically found on the SRS.

BENEFIT TO DOE

This research is designed to develop proof-of-concept for a new *in situ* remediation strategy. It addresses a DOE problem that is intractable without new knowledge. The technique may allow DOE to cleanup ^{137}Cs -contaminated wetlands in an environmentally acceptable manner--thus, winning the support and praise of Federal and State regulators, stakeholders, and citizen action groups. We think this has the potential to be an appropriate remediation strategy because it would reduce human and ecological risks, yet have no damaging effects on the wetland. If successful, this *in situ* remediation technique could be a wonderful success story for the DOE, in that, through the use of natural materials, DOE might be able to reduce the bioavailability of a major contaminant in an ecosystem that has been difficult to remediate.

MATERIALS AND METHODS

Description of Minerals

Eleven clay minerals were evaluated: two micas, two vermiculites, five illites, a kaolinite, and a smectite. The first three minerals were included to evaluate their ability to sorb and desorb Cs. Kaolinite, the dominant clay-size mineral on the SRS, was included to provide a relative value of the sorptive ability of SRS sediments versus those of the other minerals. The montmorillonite was included because it

provided an end-member to evaluate sorption and desorption trends for the progression: mica, illite, vermiculite, and smectite. General characteristics of these major mineral types are presented in Table 1, followed by characteristics of the specific minerals used in this research (Table 2). The alpha-numeric abbreviations used to refer to individual minerals throughout this report are found in the first column of Table 2.

Surface area of the minerals was obtained from the literature, but data were only available for KGa-2 and SWy-1. We estimated surface area using the BET method (Carter et al. 1986) with a Micromoretics 2000 Accelerated Surface Area and Porosimetry Analysis System. Our measurements of surface area agreed very well with the reported literature (Table 2).

Concentrations of trace elements (Cr, K, Ca, Ti, Fe, Co, Zn, As, Sr, Zr, Mo, Rb, Cd, Sn, Ba, Ag, U, and Th) in nontreated minerals were determined using x-ray fluorescence (XRF); the Spectrace 9000 system used three X-ray sources (^{109}Cd , ^{55}Fe , and ^{241}Am) and irradiated each sample for 200 sec per source (600 sec total).

Pretreatment to Remove Surface Coatings on Minerals

Adsorption and desorption of cesium is influenced by material adhering to mineral surfaces. Data on the sorption kinetics of cesium derived from minerals that have had their surface coatings removed facilitate our understanding of the mechanisms that govern cesium kinetics, and also help us in choosing a mineral specific to the remediation requirements of the SRS. Therefore, aliquots of each mineral type were treated with reagents to remove surface coatings of carbonates, free iron oxides and organic carbon using methods detailed by Kunze and Dixon (1986). as required by this method, minerals were first ground and sieved to isolate the 20- to 53- μm size fraction that was then used in all experiments. Carbonates were removed with 7 mL of 0.5 M sodium acetate (pH 5). Free iron oxides were removed with 20 mL of 0.3 M Na-citrate and 2.5 mL of 0.5 M sodium bicarbonate. The reagents and mineral samples were warmed in a water bath to 80°C and then 0.25 g of solid sodium dithionite was added. After stirring for 15 minutes the samples were removed from the water bath and a saturated NaCl solution was added as needed (approx. 5 mL) to flocculate the minerals. The samples were centrifuged, the supernate removed, and a few drops of 1M HCl were added to lower pH. Organic carbonate was removed by repeated additions of 30% H_2O_2 until frothing of samples ceased. Samples were then centrifuged and the supernate discarded. Throughout the rest of this report we refer to the mineral samples that had their surface coatings removed as "treated". Experiments were then conducted on the adsorption and desorption of ^{137}Cs by the eleven clay minerals in both treated and nontreated states.

Table 2. Selected Properties of Clay Minerals Used in this Study

Sample	Sample Location	Source	Octahedral Sheet	Particle Size (μm)	Surface Area SA (m^2/g)		Structural formula
					Measured	Literature	
Kaolinite (KGa-2)	Warren County, GA	Clay Min. Soc., Denver, CO	Di-octahedral	As received <53	22.8	23.5 ^(a)	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4^{(b)}$
Na-Montmorillonite (SWy-1)	Crook County, WY	Clay Min. Soc., Denver, CO	Di-octahedral	53 to 20	31.9	31.8 ^(a)	$\text{M}^{+}_{0.70}[(\text{Al}_{2.99}\text{Fe}^{3+}_{0.42}\text{Fe}^{2+}_{0.01})\text{Si}_{7.97}\text{Al}_{0.03}\text{O}_{20}(\text{OH})_4]^{(b)}$
Illite (IMt-1)	Silver Hill, MT	Clay Min. Soc., Denver, CO	Di-octahedral	53 to 20	32.7		
Illite (IMt-2)	Silver Hill, MT	Clay Min. Soc., Denver, CO	Di-octahedral	53 to 20	28		
Illite (Ward's)	Monroe County, NY	Ward's, Rochester, NY	Di-octahedral	53 to 20	26.4		$(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,\text{H}_2\text{O}]^{(c)}$
Illite (I-API- 35)	Gray Shale	Am. Petroleum Instit., Wash., DC	Di-octahedral	53 to 20	70.3		
Illite (I-API-Green)	Green Shale	Am. Petroleum Instit., Wash., DC	Di-octahedral	53 to 20	26.9		
Vermiculite (VTx-1)	Llano County, TX	Clay Min. Soc., Denver, CO	Tri-octahedral	53 to 20	39.5		$\text{Mg}^{2+}_{0.80}\text{Ca}^{2+}_{0.10}\text{Na}^{+}_{0.04}\text{K}^{+}_{0.01}[(\text{Mg}_{5.50}\text{Al}_{0.33}\text{Fe}_{0.04}\text{Ti}_{0.04})(\text{Si}_{5.89}\text{Al}_{2.31})\text{O}_{20}(\text{OH})_4]^{(b)}$
Vermiculite (VId-1)	Washington County, ID	Clay Min. Soc., Denver, CO		53 to 20	28.2		
Muscovite	Lord Hill, near Stoneham, ME	Ward's, Rochester, NY	Di-octahedral	53 to 20	9		$\text{K}(\text{Si}_3\text{Al})\text{Al}_2\text{O}_{10}(\text{OH})_2^{(c)}$
Biotite	Bancroft, ON, Canada	Ward's, Rochester, NY	Tri-octahedral	53 to 20	5.1		$\text{K}(\text{Mg},\text{Fe})_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2^{(c)}$

a. Web page of Clay Mineral Society – <http://www.missouri.edu/~geoscjv/SourceClay/chem.html>.

b. Weiss, Jr., 1990.

c. Dixon and Weed, 1989.

Experiment #1: Adsorption of ^{137}Cs

The goal of this experiment was to compare the ability of the various minerals to adsorb ^{137}Cs . Comparisons were made among the 11 minerals, and each mineral sample had treated aliquots in which the surface coatings were removed, as well as nontreated ones. Each treatment was replicated three times. The experiment was conducted in 50-mL centrifuge tubes, each containing 0.15 g of clay mineral. All samples were equilibrated overnight in 28 mL of filtered (0.45 μm) water from Pond B and then centrifuged (4500 rpm, 30 minutes). The equilibration step was repeated three times. The chemical composition of Pond B water is shown in Table 3. Adsorption of ^{137}Cs was initiated by adding 10 mL of ^{137}Cs -spiked Pond B water to each sample. The spiked Pond B solution contained 1718 Bq mL^{-1} (46 nCi mL^{-1}) of ^{137}Cs . Trace levels of ^{137}Cs were used to minimize competition among the dissolved Cs ions for surface sorption sites. Samples were agitated for one week with an automatic shaker, centrifuged, and a 5-mL aliquot removed for ^{137}Cs analysis. Activity of the aliquot was determined on a Packard AutoGamma NaI detector with an efficiency of 17.5%. The amount of ^{137}Cs adsorbed to the clay samples was estimated by comparing the activity of ^{137}Cs added at the beginning of the experiment to the activity in the aliquot removed one week later. The propensity for cesium to bind to minerals can be quantified with a parameter that measures the distribution of ^{137}Cs in mineral materials compared to the distribution in water. The parameter, termed a distribution coefficient (K_d), is expressed as:

$$K_d = \frac{(A_{\text{spike}} \times V_{\text{spike}}) - A_{\text{final}}(V_{\text{spike}} + V_{\text{interstitial pretreatment}})}{A_{\text{final}} \times M_{\text{clay}}} \quad (1)$$

where A_{spike} and V_{spike} are the activity concentration (Bq mL^{-1}) and volume (mL), respectively, of the ^{137}Cs solution added to the clay sample; $V_{\text{interstitial pretreatment}}$ is the volume of the interstitial solution left after the third equilibration wash (mL); M_{clay} is the clay mass (g); and A_{final} is the ^{137}Cs activity concentration in the aliquot removed at the end of the experiment (Bq mL^{-1}). Data were normalized on a mass and surface area basis.

Table 3. Analysis of Pond B Surface Water.

Sample I.D.	Date	pH	P (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Mn (mg/L)	Fe (mg/L)	Al (mg/L)	B (mg/L)
PB-1	1/24/95	6.95	<0.06	1.7	<0.40	1.23	0.43	<0.005	0.09	0.07	<0.01
PB-2	3/30/95	6.04	<0.06	1.6	<0.40	1.02	0.36	0.01	0.17	0.03	<0.01
WS.B1297	12/9/97	6.35	<0.06	1.5	<0.20	0.54	0.29	<0.001	0.27	<0.03	<0.01
WS.B5	11/20/98	6.34	<0.06	1.4	<0.20	0.91	0.35	0.09	0.55	<0.03	0.01

Experiment #2: Desorption of ^{137}Cs

The tenacity with which cesium binds to mineral surfaces varies among mineral types. Cesium can be desorbed from minerals by competing ions. An effective mineral amendment should strongly bind cesium and have minimum desorption. Ammonium ions are particularly effective at displacing cesium from the frayed edged sites of clay minerals. The purpose of Experiment #2 was to compare the ease at which ^{137}Cs desorbs from the candidate minerals in the presence of competing NH_4^+ .

Our desorption experiment was conducted on the same samples used in Experiment 1. Once the adsorption step was completed, the minerals were separated from the aqueous phase by centrifugation, and the interstitial liquid was removed by flushing the sediments with unspiked Pond B water. We then added 20 mL of 0.1 M NH_4Cl and allowed the samples to mix on an automatic shaker for two weeks. This high NH_4^+ concentration exceeds by many orders of magnitude the expected NH_4^+ concentrations on SRS surface waters, which is generally about 5 mg/L NH_4^+ . This high NH_4^+ concentration was selected to provide a worst case scenario. One potential problem with using such a high NH_4^+ concentration is that it may cause the mineral interlayers to collapse, thereby locking the sorbed Cs within the 2:1 structure. Based on results from Evans et al. (1983), it seems unlikely that this occurred in our study. Evans et al. (1983) showed a linear amount of desorption as the amount of NH_4^+ added was increased from 10^{-6} to 10^{-3} M. Had NH_4^+ caused the mineral interlayer to collapse, then the amount of Cs desorbed would have remained constant or decreased upon the addition of elevated concentrations of NH_4^+ . Following centrifugation, 5 mL of solution were removed and assayed for ^{137}Cs activity.

The amount of ^{137}Cs desorbed by each mineral was calculated as a percentage using equations 2, 3 and 4. Data were normalized on a surface area and mass basis.

$$\% \text{ desorbed} = \left(\frac{A_{\text{desorbed}}}{A_{\text{adsorbed}}} \right) \times 100 \quad (2)$$

$$A_{\text{adsorbed}} = (A_{\text{spike}} - A_A) \left(\frac{V_{\text{spike}} + V_{\text{interstitial pretreatment}}}{M_{\text{clay}}} \right) \quad (3)$$

$$A_{\text{desorbed}} = \frac{A_D(V_{\text{NH}_4\text{Cl}} + V_{\text{interstitial adsorption}}) - A_A(V_{\text{interstitial adsorption}})}{M_{\text{clay}}} \quad (4)$$

where:

- A_{desorbed} = activity of ^{137}Cs desorbed (Bq g^{-1}),
- A_{adsorbed} = activity of ^{137}Cs adsorbed (Bq g^{-1}),
- A_D = ^{137}Cs activity in equilibrium desorption solution (Bq mL^{-1}),
- A_{spike} = ^{137}Cs activity in (+) control solution (samples without sediment, Bq mL^{-1}),
- A_A = ^{137}Cs activity in adsorption solution (Bq mL^{-1}),
- V_{spike} = volume of ^{137}Cs -spike solution during adsorption experiment (mL),
- $V_{\text{NH}_4\text{Cl}}$ = volume of 0.1 M NH_4Cl added after adsorption experiment, ~20 mL (mL),
- $V_{\text{interstitial adsorption}}$ = volume of interstitial solution after adsorption experiment (mL),
- $V_{\text{interstitial pretreatment}}$ = volume of interstitial solution after pretreatment of clay with Pond B water (mL), and
- M_{clay} = mass of clay (g).

Experiment #3. Proof of Concept using Pond B sediment

Experiment #3 was a test of our hypothesis that the addition of 2:1 clays to a kaolinite-dominated system, such as occurs on the SRS, would reduce the availability of ^{137}Cs . We used sediments from Pond B, an aquatic system that was contaminated with fission products 35 year ago, and incrementally added phyllosilicate minerals to see how the mobility of ^{137}Cs was affected. From the results of the first two experiments we chose two minerals with high affinities for adsorbing ^{137}Cs (i.e. large K_d values), and low affinities for ^{137}Cs to desorb. An illite (IMt-1) and vermiculite (VId-1) were used. Each mineral was added to 20 g of moist Pond B sediment at three levels (0.01, 0.1 and 1.0 g). Desorption of ^{137}Cs from the Pond B sediments and from the mineral amended sediments were compared. Our hypothesis was that desorption would be reduced as the percentage of mineral amendments increased. Desorption was promoted by adding 20 mg L^{-1} NH_4^+ to the Pond B equilibrating solution. The experiment was conducted in 50 mL centrifuge tubes, with two replicates per treatment. Minerals were not preequilibrated with Pond B water. Samples were shaken for 2 weeks, centrifuged, and 5 mL of 0.45- μm filtered solution removed for ^{137}Cs analysis. Five experimental controls, all containing Pond B water spiked with 20 mg L^{-1} NH_4^+ , were used: 0.1 gram aliquots of the two minerals without Pond B sediment; Pond B sediments alone without mineral amendments; Pond B water without minerals and without sediment; and a chemical blank. The 5 mL removed from each sample were evaporated down, resuspended in 1 mL of 0.5 M HCl and added to 19 mL of liquid scintillation cocktail (Optiphase Trisafe). ^{137}Cs activities were determined on an ultra low-level liquid scintillation system (Quantulus, Wallac) whose lower level of detection (based on ^{90}Sr) was 0.12 Bq over a count period of 6 hours.

RESULTS

Experiment #1: Adsorption of ^{137}Cs

An experiment was conducted to evaluate the extent to which ^{137}Cs adsorbed to eleven minerals under treatments in which the surface coatings were removed, as well as, on nontreated samples. The type of mineral had a significant effect on the extent of adsorption that took place with the nontreated (Table 4) and treated (Table 5) minerals (additional information presented in Appendix A). For the non-treated

minerals, the micas, illites, vermiculites and montmorillonite had significantly larger K_d values than kaolinite ($P < 0.05$; Table 4). Two illites, IMt-1 and Ward's, had significantly greater K_d values than the remaining minerals ($P < 0.001$). The two vermiculites (VId-1 and VTx-1) had K_d values that differed by two orders-of-magnitude. The cause for this difference is that the VId-1 vermiculite almost certainly contained some fraction of mica or illite (discussed below).

Table 4. Cesium K_d and Percent Desorption Values of Non-treated Minerals^(a)

Mineral	K_d ± Std. Dev. (mL/g)	% Desorption ± Std. Dev. (%, wt/wt)	$K_{d-surface}$ ± Std. Dev. (mL/m ²)	% Desorption _{surface} ± Std. Dev. (%, wt/area; g/m ²)
Kaolinite (KGa-2)	238 ± 7 (F)	117 ± 55 (D)	10 ± 0 (F)	5.14 ± 2.40 (D)
Na-Mont. (SWy-2)	728 ± 66 (E)	90 ± 9 (A,C,D)	23 ± 2 (F)	2.82 ± 0.27 (D,E)
Illite (IMt-1)	60914 ± 1154 (C)	21 ± 1 (B)	1863 ± 353 (B,C)	0.63 ± 0.04 (A)
Illite (IMt-2)	10728 ± 3340 (A)	24 ± 6 (B)	383 ± 119 (B,D)	0.86 ± 0.20 (A)
Illite (Ward's)	29097 ± 10515 (B,C,D)	20 ± 4 (b)	1102 ± 398 (B,E)	0.77 ± 0.13 (A)
Illite (I-API-35)	9323 ± 1035 (A)	51 ± 7 (A)	133 ± 15 (A)	0.73 ± 0.10 (A)
Illite (I-API-Green)	20841 ± 2449 (A,B)	32 ± 3 (A,B)	775 ± 91 (B)	1.18 ± 0.11 (A,B)
Vermiculite (VId-1)	21959 ± 10691 (A)	4 ± 0 (E)	779 ± 379 (B)	0.15 ± 0.01 (F)
Vermiculite (VTx-1)	623 ± 47 (E)	69 ± 11 (A,D)	16 ± 1 (F)	1.75 ± 0.28 (B,E)
Mica (Muscovite)	1978 ± 320 (G)	116 ± 11 (D)	220 ± 36 (A,D)	12.94 ± 1.25 (C)
Mica (Biotite)	13464 ± 8362 (A,D)	53 ± 3 (A,B,C)	2640 ± 1640 (C,E)	10.41 ± 0.68 (C)

(a) Means within a column followed by the same capital letter are not significantly different at the 5% level of probability according to Bonferroni's multiple comparison method (Neter and Wasserman, 1974).

It was anticipated that by removing the surface coatings the dissolved ¹³⁷Cs would come into contact with the dominant mineral phase, and therefore its adsorptive behavior would be more predictive based on mineralogical considerations. Analyses showed that like the results from the nontreated samples the kaolinite and the montmorillonite had the lowest K_d values, except for the VTx-1 vermiculite (Table 5). The illites tended to have higher K_d values than either the micas or the VTx-1 vermiculite. The VId-1 vermiculite had an unexpectedly high K_d value, as was the case with the nontreated samples (Table 4).

Since adsorption processes are surface processes, the K_d values were normalized by surface area. This was accomplished by simply dividing the K_d (mL g⁻¹) values in Table 4 by the specific surface area values in Table 2. The trends between the traditional (weight normalized) and surface-normalized K_d values were quite similar with one important difference. Both mica K_{d-surf} values were appreciably greater than their respective traditional K_d values. This may be an important finding for later development of this

technology. It may prove necessary to use large particles, silt size, when remediating a Cs-contaminated wetland to limit the extent that suspended contaminated particles disperse through a wetland. The high K_{d-surf} would allow larger particles to be used without a substantial decrease in sorption efficiency.

Table 5. Cesium K_d and Percent Desorption Values of Treated Minerals^(a)

Mineral	K_d ± Std. Dev. (mL/g)	% Desorption ± Std. Dev. (%, wt/wt)	$K_{d-surface}$ ± Std. Dev. (mL/m ²)	% Desorption _{surface} ± Std. Dev. (%, wt/area; g/m ²)
Kaolinite (KGa-2)	335 ± 141 (D)	106 ± 29 (C)	15 ± 6 (G)	4.63 ± 1.26 (B)
Na-Mont. (SWy-2)	2722 ± 451 (B,C,E)	25 ± 8 (A,D)	85 ± 14 (A)	0.79 ± 0.26 (C)
Illite (IMt-1)	12301 ± 580 (A)	9 ± 4 (A,B)	376 ± 18 (A,C)	0.29 ± 0.11 (A)
Illite (IMt-2)	11712 ± 3920 (A)	5 ± 0 (B)	418 ± 140 (A,D)	0.19 ± 0.01 (A)
Illite (Ward's)	9442 ± 1840 (A)	6 ± 2 (B)	358 ± 70 (A,E)	0.21 ± 0.07 (A)
Illite (I-API-35)	10760 ± 2569 (A)	12 ± 1 (A)	153 ± 37 (A)	0.18 ± 0.02 (A)
Illite (I-API-Green)	7780 ± 1485 (A,B)	6 ± 1 (B)	289 ± 55 (A,B)	0.21 ± 0.02 (A)
Vermiculite (VId-1)	10868 ± 5648 (A)	4 ± 1 (B)	385 ± 200 (A,F,H)	0.13 ± 0.02 (A)
Vermiculite (VTx-1)	309 ± 38 (D)	60 ± 5 (C,D)	8 ± 1 (G)	1.52 ± 0.12 (B,C)
Mica (Muscovite)	5729 ± 4364 (A,E)	30 ± 2 (B)	637 ± 485 (B,E,H)	3.36 ± 0.17 (B)
Mica (Biotite)	6556 ± 3829 (A,C)	10 ± 5 (A)	1285 ± 751 (C,D,E,F)	2.61 ± 0.93 (B)

(a) Means within a column followed by the same capital letter are not significantly different at the 5% level of probability according to Bonferroni's multiple comparison method (Neter and Wasserman, 1974).

Experiment #2: Desorption of ¹³⁷Cs

Most of the ¹³⁷Cs desorbed from the kaolinite, montmorillonite, and muscovite minerals when they were put in contact with 0.1 M NH₄Cl solution (Tables 4 and 5). This result was expected for the kaolinite and montmorillonite due to the non-specific binding mechanism of cesium to these minerals. However, both micas had unexpectedly high desorption values. The cause for this is not known.

The percent Cs desorbed from all the treated samples was less than that for the nontreated samples (Table 6). This suggests that carbonate, organic, and/or Fe-oxide coatings may be weaker sorbing constituents than the underlying mineral phases. These coatings would be expected to form weaker bonds with Cs than the micas or illites. The high desorption value may, in part, be attributed to Cs sorbing to surface coatings. Overall, the nontreated minerals with the highest sorption and the lowest desorption values were the VId-1 vermiculite, and the IMt-1 and Ward's illites. An important aside is that these results suggest that the 0.1 M NH₄Cl did not cause the interlayers to collapse.

Table 6. Difference in Kd and Percent Desorption Values of Cs-137 Between Nontreated and Treated Samples

Mineral	%-Desorbed _{nontreated} - %-Desorbed _{treated} (% difference)	Kd _{nontreated} - Kd _{treated} (mL/g difference)
Kaolinite (KGa-2)	11	-97
Na-Mont. (SWy-2)	65	-1994
Illite (IMt-1)	11	48613
Illite (IMt-2)	19	-984
Illite (Wards)	15	19655
Illite (I-API-35)	39	-1436
Illite (I-API-Green)	26	13062
Vermiculite (VId-1)	1	11091
Vermiculite (VTx-1)	9	314
Mica (Muscovite)	86	-3751
Mica (Biotite)	40	6909

It was anticipated that a ranking of the minerals by the % desorption values would be: illite < mica < vermiculite << montmorillonite << kaolinite. Cesium was expected to desorb the least from the illites because they have more exposed Cs-specific sorption sites (ditrigonal sites) from frayed-edge sites (Figure 1), than mica. Vermiculite interlayers tend to expand, permitting greater access for the competing NH_4^+ ions to displace Cs. Montmorillonite has too weak a surface charge to pull the Cs into the ditrigonal opening in the tetrahedral sheet. Additionally, montmorillonite charge originates in the octahedral layer, which may be too far from the surface sorption site to pull the Cs into the ditrigonal opening. Finally, kaolinite has little charge and no site-specific Cs binding sites, thus little electrostatic or specific sorption was anticipated.

An expected trend that was not observed was biotite having a greater percentage of Cs desorbed from its surface than muscovite (Fanning et al., 1989). When the dipoles of the octahedral hydroxyls of a mica crystal are perpendicular to the basal planes (as in trioctahedral micas such as biotite), their positive dipoles are slightly closer to cations in the interlayer space. The closer dipole increases the total repulsive force felt by the Cs ions and makes the Cs ions more likely to leave the mineral. The positive dipole of the octahedral hydroxyls in dioctahedral micas, such as muscovite, is oriented toward a nearby vacant octahedral position, therefore the distance between hydroxyl protons and interlayer Cs in dioctahedral micas is larger, the anionic field interacting with Cs is stronger, and Cs is held more tightly. This reasoning is usually invoked to explain why biotite releases K, an analogue to Cs, faster than muscovite in soils, and why lower K activities in solution are required for the release of K from muscovite than from biotite.

Experiment #3. Proof of Concept using Pond B sediment

Experiment #3 was conducted to test whether or not incremental additions of the candidate minerals would reduce the mobility of ^{137}Cs contaminated, kaolinitic-dominated sediments from Pond B. Mineral selection for use in the proof-of-concept experiment was based on the results from Experiments #1 and #2. Overall, IMt-1 and VId-1, had the highest K_d values and lowest desorption values. These mineral

treatments lowered the activity released into the aqueous phase (Figure 4). The total activity released decreased with increasing amounts of mineral amendment (Figure 4). Statistical analyses indicated that the differences between the Pond B controls (Sed-cntrl) and the treatments containing 1 g of mineral were marginally significant for both VId-1 ($P=0.054$) and IMt-1 ($P = 0.08$). With only two replicates per treatment, these results are very promising. These data suggest that applying mineral amendments to SRS contaminated sediments could reduce ^{137}Cs bioavailability. We believe more replicates would have reduced the variation among treatments and improved the statistical rigor of our tests.

Figure 4. Results from proof-of-concept experiment. Data show the reduction in total activity obtained when incremental increases (0.01, 0.1 and 1.0 g) of illite (IMt1) and vermiculite (VId1) amendments were added to Pond B sediments. Columns followed by the same letter were not significantly at the 5 % level.

X-ray Fluorescence (XRF) Analysis

X-ray fluorescence (XRF) analysis of the nontreated minerals provided information about the bulk chemistry (K, Ca, Ti, Cr, Fe, Zn, As, Sr, Zr, Sb, Ba, Ag, U, and Th) of the specimens. XRF data are provided in Appendix B. XRF analyses were not conducted on treated samples because it was not known what artifacts these treatments would introduce into the analyses. Additionally, these coatings account for a small percentage of the mass of these particular minerals, likely less than 3%. Thus, it is anticipated that the elemental composition would be quite similar for both treated and nontreated samples. Two possible exceptions would be Fe, which would concentrate on the surface as oxyhydroxyl coatings, and Ca, which would be concentrated on the surface as a result of cation exchange and as part of carbonate coatings. Thus, XRF analysis of nontreated sediments may overestimate the amount of Fe and Ca on treated minerals.

Potassium, when converted to K_2O can be used as a rough approximation of the total amount micaceous material present in a sample. Fanning et al. (1989) reported that muscovite, biotite, and illite generally consists of 11.8, 10.5 and 7 % K_2O , respectively. Whereas, vermiculite, smectite, and kaolinite is expected to have essentially no K_2O . The K_2O concentrations reported in Table 7 are nearly identical to those reported by Fanning et al. (1989); muscovite, biotite, and the average illite consisted of 11.1, 10.1, and 6.8 % K_2O , respectively; kaolinite and smectite had negligible concentrations of K_2O . One notable disparity between expected and measured K_2O concentration was with VId-1 vermiculite, which contained 5% K_2O (essentially no K_2O was expected). This is a staggeringly high amount of K_2O for a vermiculite. As explained in association with Figure 1, part of the definition of a vermiculite is that K is replaced as a interlayer cation with hydrated cations, such as Ca and Mg. The high sorption and low desorption values (Tables 4 and 5), along with the high K_2O concentrations strongly suggests that some micaceous or illitic material exists in VId-1. In fact, the K_2O data suggests that there is almost certainly more micaceous or illitic material in the sample than vermiculite. X-ray diffraction analysis could provide definitive proof as to whether illites and micas are in this sample.

Correlation coefficients were calculated between the elemental composition of the minerals, and K_d and desorption values (Tables 8 and 9). In general, the treated and nontreated minerals had similar correlations. The correlation with the treated minerals were slightly greater than with the nontreated minerals, which is likely attributed to the fact that the treatments removed coatings that masked the effects of the minerals. As mentioned above, the XRF results largely reflect the elemental composition of the underlying minerals. From Table 9 it can be seen that K was positively correlated to K_d and K_{d-surf} values and negative correlated to desorption values. This is consistent with the notion that K is an indirect indicator of the amount of micaceous and illitic material in the solid phase. An important application of this information is that XRF data, which can be easily obtained with a portable field unit, may be valuable for evaluating the propensity of a sediment to sorb and retain Cs.

Table 7. Selected Elemental Concentrations (mg/kg) of Nontreated Minerals by X-ray Fluorescence Analysis

Mineral	K (% K ₂ O)	Ca	Ti	Fe	Rb
Kaolinite (KGa-2)	534 (0.1)	811	11,527	6706	BDL ^(a)
Na-Mont. (SWy-2)	5781 (0.7)	10,640	621	21,887	BDL
Illite (IMt-1)	69,604 (8.4)	10,209	4017	41,601	309
Illite (IMt-2)	67,423 (8.1)	4037	3728	38,108	218
Illite (Wards)	48,070 (5.8)	7868	4321	33,521	196
Illite (I-API-35)	42,818 (5.2)	3518	4404	39,346	197
Illite (I-API-Green)	54,668 (6.6)	9712	4605	29,978	218
Vermiculite (VId-1)	42,375 (5.1)	16,413	236	33,337	272
Vermiculite (VTx-1)	519 (0.1)	118,451	BDL	6,186	BDL
Mica (Muscovite)	92,501 (11.1)	1370	910	13,476	1599
Mica (Biotite)	83,723 (10.1)	16,581	12,120	80,203	907

(a) BDL = below detection limits

Table 8. Correlation Coefficient Values Between Mineral Elemental Concentrations and Sorption/Desorption Values of Nontreated Minerals

	K	Ca	Ti	Fe	Rb	K _d (mL/g)	Desorbed (%)	K _{d-surface} (mL/m ²)
Ca	-0.44							
Ti	-0.05	-0.02						
Fe	0.60 ^(a)	-0.30	0.37					
Rb	0.84 ^(a)	-0.20	0.04	-0.09				
K _d (mL/g)	0.40	-0.21	-0.10	0.39	-0.43			
Desorbed (%)	-0.29	0.03	0.21	-0.51	0.89 ^(a)	-0.68 ^(a)		
K _{d-surface} (mL/m ²)	0.59 ^(a)	-0.17	0.42	0.85 ^(a)	0.05	0.63 ^(a)	-0.46	
Desorption _{surface} (%/m ²)	0.35	-0.17	0.38	0.05	0.96 ^(a)	-0.41	0.71 ^(a)	0.14

(a) Significant at $\leq 5\%$ level of significance. The critical correlation coefficient for 10 degrees of freedom at $P < 0.05$ is 0.58; at $P < 0.01$ is 0.71.

Iron can exist either as coatings or in the mineral structure. Iron exists in the structure of many 2:1 minerals. It is one of the dominant divalent cations in the octahedral sheet of many illites and biotite (ideal formulae are presented in Table 1). The Fe concentration values in Table 7 are consistent with reported values (Dixon and Weed 1989). Iron concentrations were inversely correlated to desorption values and directly correlated to K_{d-surf} (Table 9). This may in part be attributed to the fact that Fe-oxides have a large propensity to sorb Cs via surface complexation (a bond between surface hydroxides and Cs), and this bond is weaker than that of the ditrigonal sites on illites and micas. However, there was not a significant ($P < 0.05$) correlation between Fe and difference in % desorption or difference in K_d values of nontreated and treated samples (Table 6). Given the multiple locations that Fe can exist in these varying mineral

assemblages, it is not surprising that significant correlations did not occur. At most, this suggests that in general the role of Fe as a coating or as an oxidized structural component did not affect sorption and desorption. Importantly, the treatments had dramatic effects on the sorption (IMt-1, Wards and I-API-Green illites) and desorption (Na-montmorillonite and muscovite) of Cs-137 from selected minerals.

Table 9. Correlation Coefficient Values Between Mineral Elemental Concentrations and Sorption/Desorption Values of Treated Minerals^(a)

	K	Ca	Ti	Fe	Rb	K _d (mL/g)	Desorbed (%)	K _{d-surf} (mL/m ²)
Ca	-0.44							
Ti	-0.05	-0.02						
Fe	0.60 ^(b)	-0.30	0.37					
Rb	0.84 ^(b)	-0.20	0.04	-0.09				
K _d (mL/g)	0.64 ^(b)	-0.47	-0.36	0.55	-0.77 ^(b)			
Desorption (%)	-0.62 ^(b)	0.29	0.50	-0.61 ^(b)	0.92 ^(b)	-0.82 ^(b)		
K _{d-surf} (mL/m ²)	0.79 ^(b)	-0.25	0.34	0.80 ^(b)	0.60 ^(b)	0.29	-0.42	
Desorbed (%/m ²)	-0.17	-0.04	0.59 ^(b)	-0.30	0.97 ^(b)	-0.68 ^(b)	0.84 ^(b)	0.07

(a) XRF elemental analyses were conducted using nontreated mineral samples. XRF analysis samples the entire mineral, not just the surface; thus the difference in the elemental composition as a result of removing the coatings would likely be minimal for all elements except Ca (the dominant exchangeable cation in this system) and Fe (the dominant element in oxyhydroxide coatings).

(b) Significant at $\leq 5\%$ level of significance. The critical correlation coefficient for 10 degrees of freedom at $P < 0.05$ is 0.58; at $P < 0.01$ is 0.71.

Rubidium is a monovalent alkaline cation that is slightly smaller than Cs⁺, but is larger than K⁺ and NH₄⁺. Rubidium concentrations were highly correlated to all four sorption/desorption parameters (Table 9). This has not been reported before. Especially difficult to explain is why mineral Rb concentrations are directly correlated to K_{d-surf} and inversely correlated to the traditional K_d construct. Given these exceptionally strong correlations, additional research needs to be conducted to explain this result.

CONCLUSIONS

Cesium-137 has contaminated a large area of the wetlands on the Savannah River Site. During the summer, when the hypolimnion become anoxic, about 1% of the ¹³⁷Cs that is bound to the sediments is released into the overlying water (Evans et al., 1983, Whicker et al. 1990). The cause for the release is likely the combined effect of increased NH₄⁺ concentrations and the dissolution of Fe(III)-oxides during anoxic conditions. Ammonium can displace ¹³⁷Cs from sorption sites on sediments, and Fe(III)-oxides can release sorbed Cs upon reduction to Fe(II). This annual release of Cs is appreciably more mobile and more accessible to the biosphere than that which is bound to the sediments. Although representing only a small percentage of the total inventory, the released ¹³⁷Cs is sufficient to cause measurable concentrations in all components of the wetlands (e.g. water, plants, aquatic insects, fish, etc.), and results in ¹³⁷Cs being the primary driver in human and ecological risks on the SRS (Whicker et al. 1993). Remediation of the contaminated wetlands is problematic because current techniques destroy the sensitive ecosystem and

generate a higher dose to workers. To address the problem, we proposed a non-intrusive, *in situ* technology to sequester ^{137}Cs in sediments. The technology involves introducing illitic minerals to the surface of Cs-contaminated waters. Such minerals characteristically have a strong affinity for Cs, and once bound, tend to hold Cs tenaciously. These characteristics are opposite those of the predominant mineral on the SRS: kaolinite. The mineral amendments would capture ^{137}Cs during its annual summer release, thereby reducing transport to the biota and providing a non-intrusive remediation solution.

As an initial test of our hypothesis, three experiments were conducted. The first two quantified adsorptive and desorptive properties of eleven candidate mineral amendments. The intent was to identify specific minerals that could be used for the proposed technology. An important additional objective was to identify mineral specifications so that quarried minerals could be appropriately chosen if the technology is scaled-up to a field application. The third experiment was a proof-of-concept of the proposed technology, whereby we incrementally added candidate minerals to kaolinitic-dominated sediments of Pond B to see if mobility of ^{137}Cs was reduced.

The most important conclusions from the study of cesium adsorption and desorption were:

- Several clay minerals (IMt-1, IMt-2, Ward's, Vid-1) were identified to have high Cs- K_d values and low Cs-desorption values. Cs- K_d values of $>10,000 \text{ mL g}^{-1}$ and % desorption of $<10\%$ (under extremely harsh experimental conditions) can be expected from these minerals.
- Minerals treated to remove carbonates, free iron oxides, and organic coatings had consistently, and in some cases appreciably, less Cs desorption than untreated minerals.
- Specific mineral characteristics were identified and should be used when choosing quarried minerals for this technology. The quarried minerals should contain illite (not kaolinite, smectite, or biotite) with moderate levels of K_2O , and should contain low concentrations of surface coatings.

The most important conclusion from the proof-of-concept study was:

- Incremental additions of two clay minerals (IMt-1 and Vid-1) to Pond B sediments, contaminated over 35 years ago, appreciably reduced desorption of ^{137}Cs . The data revealed a trend of reduced total soluble activity with increasing amounts of mineral amendment.

One intention of this study was to provide information regarding a "go/no go" decision for future work. Since the proof-of-concept was successful and several minerals were identified as potential candidates for this technology, a "go" decision was made. Future work should address the following issues.

- *Limnocorral Study:* All the experiments to date have been bench-top, laboratory-scale applications. A replicated, mesocosm approach using lake limnocorrals is needed to quantify the ability of the mineral amendments to decrease ^{137}Cs mobility under natural conditions.
- *Water Quality and Ecological Impact Study:* Impact of the proposed technology on the environment needs to be quantified; including changes to water quality, and the biological effects of the mineral amendments on plants, aquatic insects, and fish populations.

- *Particle-size Study*: Examine the influence of particle size on ^{137}Cs adsorption and desorption. If particle size is too small the mineral may be overly dispersive in the environment, if too large, the effective surface area for ^{137}Cs adsorption would be reduced.
- *Cradle-to-Grave Cost Analysis of Technology*: Consider the engineering aspects of applying mineral amendments and quantify the costs.
- *Specifications for Quarried Minerals*: Finally, additional characterization of the minerals would further help in identifying important specifications for the quarried minerals. X-ray analysis would identify and semi-quantify the various components of these mineral assemblages. Measurement of the concentration of frayed-edge sites (Cremers et al. 1988) would quantify the number of exchange sites that "irreversibly sorb" (e.g. ditrigonal sorption sites) versus reversibly sorb (e.g., cation exchange sites) ^{137}Cs on illites and micas.

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APPENDICES

Appendix A. K_d and % Desorption Values For Treated and Non-treated Minerals.

Mineral	Treated (yes/no)	K_d (mL/g)	Mean K_d (mL/g)	Std. Dev. K_d (mL/g)	Desorbed (%)	Mean Desorbed (%)	Std. Dev. Desorbed (%)
Illite (IMt-1)	Yes	12948	12301	580	10.6	9.4	3.7
Illite (IMt-1)	Yes	12124			12.3		
Illite (IMt-1)	Yes	11829			5.2		
Illite (IMt-2)	Yes	9382	11712	3920	5.6	5.2	0.4
Illite (IMt-2)	Yes	9517			4.9		
Illite (IMt-2)	Yes	16238			5.2		
Illite (Ward's)	Yes	7695	9442	1840	3.9	5.6	1.7
Illite (Ward's)	Yes	11363			5.7		
Illite (Ward's)	Yes	9267			7.4		
Illite (I-API-35)	Yes	12392	10760	2569	11.3	12.3	1.1
Illite (I-API-35)	Yes	12088			12.2		
Illite (I-API-35)	Yes	7799			13.5		
Illite (I-API-Green)	Yes	6693	7780	1485	5.6	5.6	0.5
Illite (I-API-Green)	Yes	7174			6.1		
Illite (I-API-Green)	Yes	9472			5.1		
Na. Mont. (SWy-2)	Yes	2545	2722	451	17.2	25.3	8.2
Na. Mont. (SWy-2)	Yes	2386			33.6		
Na. Mont. (SWy-2)	Yes	3235			25.1		
Kaolinite (KGa-2)	Yes	497	335	141	73.2	105.6	28.7
Kaolinite (KGa-2)	Yes	253			127.6		
Kaolinite (KGa-2)	Yes	255			116.1		
Vermiculite (VId-1)	Yes	4972	10868	5648	3.5	3.6	0.5
Vermiculite (VId-1)	Yes	11404			3.2		
Vermiculite (VId-1)	Yes	16229			4.2		
Vermiculite (VTx-1)	Yes	268	309	38	63.6	60.2	4.9
Vermiculite (VTx-1)	Yes	315			62.4		
Vermiculite (VTx-1)	Yes	343			54.6		
Mica (Muscovite)	Yes	4221	5729	4364	31.9	30.3	1.5
Mica (Muscovite)	Yes	10647			28.9		
Mica (Muscovite)	Yes	2319			29.9		
Mica (Biotite)	Yes	4987	6556	3829	18.6	13.3	4.7
Mica (Biotite)	Yes	10919			9.4		
Mica (Biotite)	Yes	3760			11.9		
Illite (IMt-1)	No	58837	60914	11554	20.1	20.6	1.4
Illite (IMt-1)	No	73366			19.4		
Illite (IMt-1)	No	50539			22.2		
Illite (IMt-2)	No	12745	10728	3340	19.6	24.0	5.7
Illite (IMt-2)	No	6873			30.4		
Illite (IMt-2)	No	12566			21.9		

Appendix A (Continued)

Mineral	Treated (yes/no)	K _d (mL/g)	Mean K _d (mL/g)	Std. Dev. K _d (mL/g)	Desorbed (%)	Mean Desorbed (%)	Std. Dev. Desorbed (%)
Illite (Ward's)	No	41181	29097	10515	19.9	20.4	3.5
Illite (Ward's)	No	22031			24.1		
Illite (Ward's)	No	24080			17.1		
Illite (I-API-35)	No	10318	9323	1035	52.7	51.0	7.4
Illite (I-API-35)	No	9399			43.0		
Illite (I-API-35)	No	8252			57.4		
Illite (I-API-Green)	No	22548	20841	2449	30.2	31.7	3.0
Illite (I-API-Green)	No	21940			29.8		
Illite (I-API-Green)	No	18035			35.1		
Na. Mont. (SWy-2)	No	690	728	66	95.6	89.8	8.8
Na. Mont. (SWy-2)	No	804			79.8		
Na. Mont. (SWy-2)	No	690			94.1		
Kaolinite (KGa-2)	No	233	238	7	156.2	117.2	54.6
Kaolinite (KGa-2)	No	245			54.8		
Kaolinite (KGa-2)	No	234			140.6		
Vermiculite (VId-1)	No	32707	21959	10691	4.7	4.3	0.4
Vermiculite (VId-1)	No	11326			3.9		
Vermiculite (VId-1)	No	21844			4.3		
Vermiculite (VTx-1)	No	658	623	47	60.9	69.1	10.9
Vermiculite (VTx-1)	No	571			81.5		
Vermiculite (VTx-1)	No	641			64.9		
Mica (Muscovite)	No	1626	1978	320	126.5	116.4	11.2
Mica (Muscovite)	No	2251			104.3		
Mica (Muscovite)	No	2057			118.4		
Mica (Biotite)	No	9647	13464	8362	49.1	53.1	3.5
Mica (Biotite)	No	23054			54.9		
Mica (Biotite)	No	7692			55.3		

Appendix B. XRF Elemental Analysis (All Values Not Presented Are Below Detection Limit).

Illite (IMt-1)

Element	Concentration (mg/kg)	Std. Dev. (mg/kg)
CrHI	166	106
K	69605	379
Ca	10209	143
Ti	4017	82
CrLO	198	53
Fe	41601	372
Ni	135	38
Zn	92	15
As	18	11
Sr	225	6
Zr	99	3
Rb	309	10
Ba	359	8
Ag	20	18
U	15	6
Th	15	3

Vermiculite (VIId-1)

Element	Concentration (mg/kg)	Std. Dev. (mg/kg)
K	42375	299
Ca	16413	149
Ti	236	40
CrLO	321	44
Mn	3872	187
Fe	33337	320
Cu	61	18
Zn	974	30
As	24	10
Rb	272	9
Ba	304	7
U	7	5

Appendix B (Continued)

Illite (IMt-2)

Element	Concentration (mg/kg)	Std. Dev. (mg/kg)
CrHI	138	102
K	67423	374
Ca	4037	115
Ti	3728	79
CrLO	145	52
Fe	38108	352
Co	207	119
Zn	88	15
As	30	11
Sr	135	5
Zr	126	3
Mo	5	3
Rb	218	9
Cd	88	26
Sn	37	16
Ba	187	6
Ag	59	17
U	16	5
Th	25	3

Mica (Muscovite)

Element	Concentration (mg/kg)	Std. Dev. (mg/kg)
K	92501	436
Ca	1370	121
Ti	910	42
CrLO	366	45
Fe	13476	213
Cu	47	17
Zn	152	15
As	199	12
Sr	3	2
Rb	1599	21
Cd	26	19
Sn	179	14
U	204	13
Th	106	6

Appendix B (Continued)

Na-Montmorillonite

Element	Concentration (mg/kg)	Std. Dev. (mg/kg)
K	5781	126
Ca	10640	105
Ti	621	37
CrLO	158	38
Fe	21887	241
Zn	135	14
As	46	10
Sr	310	6
Zr	172	3
Sb	8	7
Ba	79	4
Ag	19	13
U	58	5
Th	82	4

Illite (Ward's)

Element	Concentration (mg/kg)	Std. Dev. (mg/kg)
CrHI	103	97
K	48070	317
Ca	7868	120
Ti	4321	83
Fe	33521	322
Zn	126	15
As	47	11
Sr	75	4
Zr	157	3
Rb	196	8
Sb	16	9
Ba	207	6
Ag	40	16
U	26	5
Th	21	3

Mica (Biotite)

Element	Concentration (mg/kg)	Std. Dev. (mg/kg)
K	83723	415
Ca	16581	175
Ti	12120	134
Mn	2128	198
Fe	80203	547
Zn	702	30
As	99	13
Sr	173	6
Rb	907	19
Sb	20	10
Ba	559	10
U	72	8
Th	45	4

Vermiculite (VTx-1)

Element	Concentration (mg/kg)	Std. Dev. (mg/kg)
K	519	148
Ca	118451	326
CrLO	338	45
Mn	257	92
Fe	6186	145
Zn	63	14
Sr	44	3
Zr	6	1
Mo	4	2
Sb	15	9
Ba	7	2
Ag	44	17
U	14	3

Appendix B (Continued)

Illite (I-API-35)

Element	Concentration (mg/kg)	Std. Dev. (mg/kg)
CrHI	175	103
K	42818	300
Ca	3518	95
Ti	4405	83
CrLO	79	52
Fe	39346	346
Co	162	116
Cu	51	18
Zn	166	17
As	63	12
Sr	154	5
Zr	186	4
Mo	4	3
Rb	197	8
Cd	36	25
Ba	248	6
Ag	25	17
U	25	5
Th	15	3

Kaolinite (KGa-2)

Element	Concentration (mg/kg)	Std. Dev. (mg/kg)
K	534	64
Ca	812	38
Ti	11527	115
Fe	6705	134
Zn	117	13
As	31	9
Sr	59	3
Zr	187	3
Pb	7	6
Sb	6	6
Ba	16	2
U	41	3
Th	49	3

Appendix B (Continued)

Illite (I-API-Green)

Element	Concentration (mg/kg)	Std. Dev. (mg/kg)
K	54669	338
Ca	9713	132
Ti	4605	86
Mn	166	110
Fe	29978	307
Cu	124	20
Zn	140	16
As	59	11
Sr	88	4
Zr	152	3
Rb	218	9
Cd	36	20
Sn	25	13
Ba	149	5
U	30	5
Th	14	3

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