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**Partitioning of Cesium-137 and Other Gamma-Emitting Radionuclides to SRS Sediments  
Recovered from Field Lysimeter Experiments at the Savannah River Site**

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## 1. Introduction

Defense operations conducted by the U.S. Department of Energy (DOE) have left a legacy of radioactive wastes that present a significant health hazard to the U.S. public. Cementitious or vitrified (e.g., glassy) wasteforms, which chemically incorporate nuclear waste, represent two possible strategies to immobilize and to prevent public exposure to the waste. Compared with cementitious wasteforms, vitrified wasteforms offer several advantages, including high waste loadings, small form factors, and superior chemical resistance, which is expected to inhibit alteration and release of radioactive materials from the wasteform during long-term storage in subsurface geological environments.<sup>1,2</sup> Therefore, many DOE facilities have elected to use vitrification for the immobilization of nuclear wastes, particularly those classified as high-level wastes (HLW), which contain various highly-radioactive materials, including gamma-emitting fission products. Although numerous studies have confirmed with laboratory or field-scale experiments the high-durability and low alteration rates of real or simulated vitrified wasteforms,<sup>3-8</sup> few studies<sup>7,9,10</sup> have assessed the long-term behavior of radioactive materials released from these wasteforms during exposure to environmentally-relevant conditions, inhibiting efforts to understand the health risks associated with the long-term burial and storage of vitrified nuclear waste.

To address this need, we examined the sorption behavior of cesium-137 (<sup>137</sup>Cs), a gamma-emitting radionuclide, after release from a fragment of vitrified HLW emplaced in a field-scale lysimeter buried in the vadose zone. This project was initiated at the Savannah River Site (SRS) in 1981 with the specific goal of quantifying radionuclide release and transport within the vadose zone. The lysimeters—52 L plastic carboys filled with local SRS sediment and containing various radioactive-contaminant source materials—were buried in the vadose zone and exposed to natural weather conditions, including precipitation. After a period of 11 or more years, the lysimeters were either removed for detailed analysis of radionuclide transport within the lysimeter sediment or capped with a cement cover and left in place in the field. A second lysimeter project, the Radionuclide Field Lysimeter Experiment (RadFLEX), was initiated at the SRS in 2012 to further advance an understanding of radionuclide fate and transport in the vadose zone. For comparison with data from the original 1981 lysimeter project, we also quantified the sorption of several gamma-emitting radionuclides from a control lysimeter in the RadFLEX project.

This report quantifies partition coefficients ( $K_d$ ) of gamma-emitting radionuclides to SRS sediments after long-term burial in the vadose zone and exposure to natural conditions. Two lysimeter experiments from the SRS were examined: lysimeter M2 from the original 1981 project, which contained a fragment of vitrified HLW; and a control lysimeter, L26, from the RadFLEX project, which contained a suite of gamma-emitting radionuclides (<sup>60</sup>Co, <sup>137</sup>Cs, <sup>133</sup>Ba, and <sup>152</sup>Eu). Partition coefficients measured for <sup>60</sup>Co, <sup>137</sup>Cs, <sup>133</sup>Ba, and <sup>152</sup>Eu for the control lysimeter sediments and the partition coefficient for <sup>137</sup>Cs for lysimeter M2 are reported. The larger  $K_d$  values reported here for <sup>137</sup>Cs and <sup>152</sup>Eu compared with short-term laboratory experiments suggest that increased contact time with sediments (aging) increases the sorption affinity of Cs and Eu. However, no significant difference was observed between the <sup>137</sup>Cs  $K_d$  values measured for the M2 lysimeter sediments and the L26 lysimeter sediments, even though the M2 lysimeter remained in the vadose zone for a longer period of time than the L26 lysimeter. Because these experiments directly probe

the impact of natural weather conditions on the transport of gamma-emitting radionuclides within SRS sediments, we expect that the reported  $K_d$  values will decrease uncertainties associated with predicting radionuclide behavior in the subsurface during long-term storage of nuclear waste at the SRS.

## 2. Background

### *M2 Lysimeter*

A cylinder of vitrified HLW (1.3 cm length  $\times$  1.3 cm diameter) was buried  $\sim$ 21.6 cm below the sediment surface in a lysimeter located  $\sim$ 11 m above the water table on the SRS.<sup>9</sup> As such the waste was exposed to saturated and unsaturated conditions as controlled by local rainfall and weather. The glass cylinder contained a range of radionuclides, including  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ ,  $^{137\text{m}}\text{Ba}$ , and  $^{154}\text{Eu}$  with estimated activities of 23, 23, 21, and 16  $\mu\text{Ci g}^{-1}$ , respectively.<sup>9</sup> The lysimeter was exposed to natural conditions for 11 years and capped for 13 years.<sup>9</sup> After this period of 24 years, the vitrified waste cylinder was recovered by coring. A previous analysis of the initial sediment core revealed that the glass cylinder had fractured, either during emplacement in the field or during recovery of the initial core. However, no additional glass fragments were found during the additional sampling of the lysimeter sediments, indicating that the wastefrom cylinder itself had not moved significantly from its original burial location within the lysimeter. In this work, sediments from segments M2-1305 and M2-1309 were used in desorption experiments. Sample M2-1305 was recovered from 26.0 to 27.9 cm below the source location and M2-1309 was recovered from 20.4 to 21.5 cm below the source. Thus, these samples are representative of down-gradient sediments where radionuclides leached from the wastefrom were re-adsorbed to the sediments.

### *L26 Lysimeter*

In contrast to the original 1981 lysimeter project, the RadFLEX lysimeters were constructed from PVC pipe (10 cm I.D.  $\times$  61 cm L, 4.9 L total volume). A full description of the lysimeter design and setup is provided in Roberts et al.<sup>11</sup> The control lysimeter, L26, contained a suite of gamma-emitting radionuclides ( $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ ,  $^{133}\text{Ba}$ , and  $^{152}\text{Eu}$ ) that were pipetted from an aqueous solution and dried onto a glass-fiber filter paper. The filter paper was inserted at 25.4 cm from the top of the lysimeter as the radionuclide source. The L26 lysimeter experiment was initiated on July 5, 2012, and the effluent from L26 was monitored for the release of radionuclides until September 14, 2016, at which point the lysimeter was capped and removed (September 15, 2016) from the RadFLEX installment to perform a non-destructive 1D gamma-spectroscopy analysis. There was also a brief two-month period in 2013 in which the L26 lysimeter was capped to prevent further intrusion of rainfall. During active monitoring of the effluent from this lysimeter, only  $^{60}\text{Co}$  was detected at concentrations greater than the detection limit.<sup>12</sup> Three sediment samples from different depths within the L26 lysimeter were examined here: L26-16, L26-17, and L26-18, which were sediments located at 29.5, 30.7, and 31.9 cm, respectively, from the top of the lysimeter.

## 3. Materials and Methods

### *Desorption experiment*

Dried L26 and M2 lysimeter sediment samples received from the SRS were mixed with NaCl to extract available radionuclides. Sediment-to-solution ratios of 1/10, 2/20, and 4/40 were used. In

brief, one, two, or four grams of the dried sediment from each lysimeter sample was extracted with 10, 20, or 40 mL of 0.01 M NaCl on a reciprocating shaker for 30 days. All extractions were completed in triplicate. After 30 days, the pH was measured, and the samples were centrifuged at 3000 rpm for 30 minutes. A 9 mL aliquot of each supernatant was transferred to a 20 mL polyethylene LSC vial for analysis by gamma spectroscopy; this containment ensured consistent geometry between all samples during gamma counting. The results for the 1/10 sediment-solution ratio are omitted from this report because the measured radioactivities were below detection limits.

### ***Analysis of Gamma Emitting Radionuclides***

Each of the extraction samples were analyzed by gamma spectroscopy using a high purity germanium detector (HPGe, GC-1818, Canberra Industries, Inc). For the extraction samples, energy and efficiency calibrations for the HPGe detector were performed using 9 mL of a NIST traceable  $^{152}\text{Eu}$  stock solution contained within a 20 mL polyethylene LSC vial. This  $^{152}\text{Eu}$  liquid standard was counted for 4 h (14400 s). The same geometry (9 mL in 20 mL LSC vial) and counting time (4 h) was used to measure the activity in each extraction sample. The energy calibration curve for the 9 mL liquid sample geometry is shown below (Figure 1).

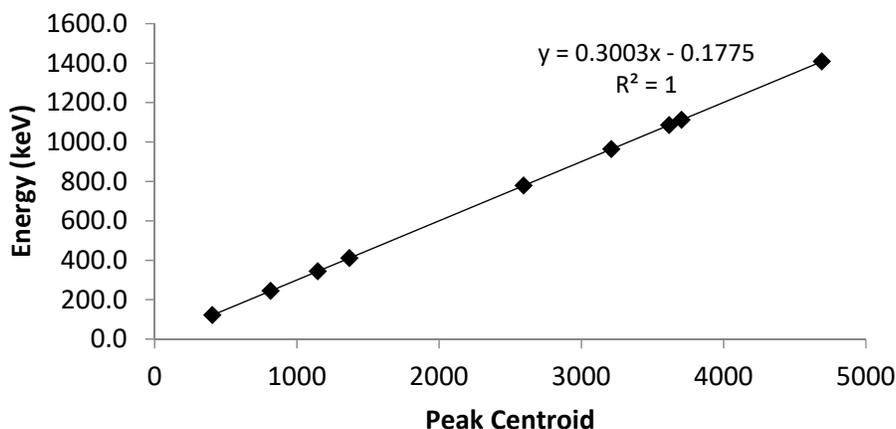


Figure 1: HPGe energy calibration using the NIST certified  $^{152}\text{Eu}$  solution (9 mL) contained in a 20 mL LSC vial.

The total activity,  $A_{total}$  ( $\text{Bq kg}^{-1}$  sediment), in each of the dried sediments was originally reported by the Savannah River National Laboratory (SRNL). However, the measured  $^{133}\text{Ba}$  activities in the extraction solutions for the L26 lysimeter sediment samples were larger than the total activities in the sediments as reported by SRNL, yielding negative  $^{133}\text{Ba}$   $K_d$  values. Therefore, we re-measured  $A_{total}$  for each of the dried sediment samples, except the M2-1305 sample, which was consumed during the desorption experiments. For these measurements, the energy and efficiency of the HPGe detector were calibrated by counting a sediment standard sealed in a polystyrene petri dish for 9.6 h (34697 s). This standard was prepared by mixing 43 Bq of the NIST traceable  $^{152}\text{Eu}$  stock solution with 5 g of clean SRS sediment. The same sample geometry (5 g sediment in sealed petri dish) was used to measure the total activity in each dried sediment sample. Counting times for each of the dried sediment samples varied from approximately 6 min to 21 h, depending on expected activities. The re-measured total activities for each of the gamma-emitting isotopes in the

L26 lysimeter sediments are approximately 5-times greater than the activities reported by the SRNL. However, the total  $^{137}\text{Cs}$  activity for the M2-1309 sediment sample reported by the SRNL (3066 Bq kg<sup>-1</sup>) is similar to the total activity measured here (3633 Bq kg<sup>-1</sup>), suggesting that the total activities for the M2 lysimeter samples reported by the SRNL, which were measured at a different time than those of the L26 lysimeter samples, are accurate. Because the M2-1305 sample was consumed during the desorption experiment, the SRNL reported  $A_{total}$  for  $^{137}\text{Cs}$  was used to calculate the  $K_d$  value for this sample. Continued investigation of the discrepancy between the  $A_{total}$  values measured here and those reported by the SRNL revealed that the SRNL incorrectly calculated  $A_{total}$  for the L26 sediment samples.\* The SRNL calculations divided the sediment activities (Bq) by the sample mass (~5 g) twice (i.e., Bq kg<sup>-1</sup> kg<sup>-1</sup>), yielding  $A_{total}$  values that were effectively ~5-times smaller than those measured in this work.

### ***Determination of Sediment Partition Coefficients***

The list of gamma decay energies and associated intensities used to determine the activities of  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ ,  $^{133}\text{Ba}$ , and  $^{152}\text{Eu}$  are shown in Table 1. The gamma energies in Table 1 were chosen because they are emitted with the highest intensities. Activities of  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$ ,  $^{133}\text{Ba}$ , and  $^{152}\text{Eu}$  were calculated based on the count rates associated with the gamma energies in Table 1; errors are reported as the standard deviation of triplicate measurements. The minimum detectable concentration (MDC) for each radionuclide given in Table 1 was calculated as shown below:

$$L_D = 2.71 + 4.65\sqrt{b} ,$$

$$\text{MDC (Bq L}^{-1}\text{)} = \frac{L_D}{\epsilon \cdot f \cdot t \cdot V_{gs}} ,$$

where  $L_D$  is the limit of detection defined by Currie,<sup>13</sup>  $b$  is the number of background counts in a defined spectral region of interest (ROI),  $\epsilon$  and  $f$  are the detection efficiency and decay fraction (intensity), respectively, for each specific gamma ray detected (Table 1),  $t$  is the total counting time (14400 s), and  $V_{gs}$  is the sample volume (9 mL) of each standard or extract solution analyzed by gamma spectroscopy.

*Table 1: Gamma decay energies and associated decay fractions ( $f$ ) and detection efficiencies ( $\epsilon$ ) for each radionuclide quantified in this work.*

<b>Radionuclide</b>	<b>Decay Energy (keV)</b>	<b><math>f</math></b>	<b><math>\epsilon</math></b>	<b>MDC (Bq L<sup>-1</sup>)</b>
$^{137}\text{Cs}$	661	0.851	0.0111	16.94
$^{60}\text{Co}$	1173	0.999	0.0069	16.87
$^{133}\text{Ba}$	356	0.621	0.0186	9.43
$^{152}\text{Eu}$	121	0.285	0.0400	29.77

\* Personal communications between Kimberly Roberts (SRNL), Dan I. Kaplan (SRNL), Shanna L. Estes (Clemson), and Brian A. Powell (Clemson) on July 20, 2020.

Radionuclide activities ( $A_{extract}$ ) measured in each of the extract solutions were calculated as shown below:

$$A_{extract}(\text{Bq L}^{-1}) = \frac{\text{gamma counts} - b}{\epsilon \cdot f \cdot t \cdot V_{gs}}$$

Partition coefficients ( $K_d$ ) for  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$ ,  $^{133}\text{Ba}$ , and  $^{152}\text{Eu}$  were calculated as shown below:

$$K_d(\text{mL g}^{-1}) = \frac{A_{sediment}(\text{Bq g}^{-1})}{A_{extract}(\text{Bq mL}^{-1})} = \frac{A_{total} - \left(\frac{A_{extract} \cdot V_t}{m_{sediment}}\right)}{A_{extract}}$$

where  $A_{sediment}$  ( $\text{Bq g}^{-1}$  sediment) is the radionuclide activity remaining in the lysimeter sediments after the 30-day extraction,  $A_{total}$  ( $\text{Bq g}^{-1}$  sediment) is the total radionuclide activity measured in the dry sediment,  $V_t$  is the total volume of the extraction solution (10, 20, or 40 mL), and  $m_{sediment}$  is the total mass of dried sediment used in the extraction (1, 2, or 4 g).

Using the minimum detectable concentrations of each isotope based on the aqueous phase measurements in Table 1 and the total soil phase concentration of each isotope (Appendix Table A.1), a maximum detectable  $K_d$  value can be determined as:

$$K_{d,maximum}(\text{L kg}^{-1}) = \frac{[A_{initial,soil}] \left(\frac{\text{Bq}}{\text{kg}}\right)}{MDC_{aqu} \left(\frac{\text{Bq}}{\text{L}}\right)}$$

As these values are dependent on the soil phase concentration of each isotope, separate values are reported for each source. These are provided to allow comparison with the  $K_d$  values determined from experimental data.

#### 4. Results

Cesium-137 was detected in all of the dried L26 sediment samples and in most of the extraction solutions from these samples, except those extracted using a sediment-to-solution ratio of 1/10 (Table 2). The  $^{137}\text{Cs}$   $K_d$  values for the L26 lysimeter range from 1896 to 2573  $\text{mL g}^{-1}$ . These  $K_d$  values are 1000-times larger than those reported from seven-day laboratory sorption experiments with similar SRS sediments,<sup>14</sup> suggesting that increased contact time, 5 y vs. 7 d, with lysimeter sediments results in stronger sorption of Cs to mineral surfaces. This “aging” process has been linked to the slow exchange and fixation of Cs onto interlayer sites in 2:1 clay minerals.<sup>15–19</sup>

Cesium-137 was also detected in two of the M2 sediments, but only in one of the extract solutions (Table 3). The  $^{137}\text{Cs}$   $K_d$  value determined for the M2-1305 lysimeter sediment sample is  $\sim 2051 \text{ mL g}^{-1}$ . This  $K_d$  value is similar to that measured for the L26 lysimeter sediments, despite the longer (24 y vs. 5 y) deployment time of the M2 lysimeter. This finding may indicate that the “aging” process maximizes after a few years and that additional exposure to natural conditions does not further enhance  $^{137}\text{Cs}$  adsorption.

Table 2: Average  $^{137}\text{Cs}$  extraction activities, total activities, and  $K_d$  values for lysimeter L26. Numbers in parentheses are the standard deviation to the means, and “–” activities are below detection limits.

Sample name	Solid/Solution ratio (kg/L)	pH	Extract activity (Bq/L)	Total activity (Bq/kg)	$K_d$ (mL/g)	Maximum detectable $K_d$ (mL/g)
L26-18	4/40	4.88 (0.03)	-	$1.53 \times 10^4$	-	$9.02 \times 10^2$
L26-17	4/40	4.89 (0.01)	114.7 (17.8)	$2.63 \times 10^5$	2324 (389)	$1.55 \times 10^4$
L26-16	4/40	4.89 (0.03)	777.6 (87.3)	$1.99 \times 10^6$	2573 (302)	$1.18 \times 10^5$
L26-18	2/20	4.84 (0.02)	-	$1.53 \times 10^4$	-	$9.02 \times 10^2$
L26-17	2/20	4.87 (0.03)	127.5 (15.0)	$2.63 \times 10^5$	2068 (245)	$1.55 \times 10^4$
L26-16	2/20	4.90 (0.04)	1070.8 (237.0)	$1.99 \times 10^6$	1896 (422)	$1.18 \times 10^5$

Table 3: Average  $^{137}\text{Cs}$  extraction activities, total activities, and  $K_d$  values for lysimeter M2. Numbers in parentheses are the standard deviation to the means, and “–” activities are below detection limits.

Sample name	Solid/Solution ratio (kg/L)	pH	Extract activity (Bq/L)	Total activity (Bq/kg)	$K_d$ (mL/g)	Maximum detectable $K_d$ (mL/g)
M2-1309	4/40	5.06 (0.02)	-	$3.63 \times 10^3$	-	$2.15 \times 10^2$
M2-1305	4/40	5.97 (0.04)	14.9 <sup>a</sup>	$3.07 \times 10^{4b}$	2051 <sup>a</sup>	$1.81 \times 10^3$

<sup>a</sup>No standard deviation is given here because  $^{137}\text{Cs}$  was detected in only one of the replicate leachate samples from sediment M2-1305; thus, no  $K_d$  value could be calculated for the replicate in which  $^{137}\text{Cs}$  was not detected.

<sup>b</sup>Total activity reported by Savannah River National Laboratory collaborator Daniel I. Kaplan upon delivery of sediment.

The gamma-emitting radionuclides  $^{60}\text{Co}$ ,  $^{133}\text{Ba}$ , and  $^{152}\text{Eu}$  were detected in all of the dried L26 lysimeter sediment samples and in most of the extraction solutions. The  $^{60}\text{Co}$   $K_d$  values for the L26 lysimeter range from 18.5 to 38.7 mL g<sup>-1</sup> (Tables 4). Consistent with the earlier identification of  $^{60}\text{Co}$  in the L26 lysimeter effluent,<sup>12</sup> the small  $K_d$  values determined in this work confirm that  $^{60}\text{Co}$  does not adsorb strongly to SRS sediments. Furthermore, the  $K_d$  values measured here are similar to those reported in a seven-day laboratory sorption experiment,<sup>14</sup> indicating that, unlike the behavior observed for Cs, increased contact time does not increase the affinity of  $^{60}\text{Co}$  to the SRS sediments.

Table 4: Average  $^{60}\text{Co}$  extraction activities, total activities, and  $K_d$  values for lysimeter L26. Numbers in parentheses are the standard deviation to the means.

Sample name	Solid/Solution ratio (kg/L)	pH	Extract activity (Bq/L)	Total activity (Bq/kg)	$K_d$ (mL/g)	Maximum detectable $K_d$ (mL/g)
L26-18	4/40	4.88 (0.03)	1696.8 (416.7)	$7.88 \times 10^4$	38.7 (13.9)	$4.67 \times 10^3$
L26-17	4/40	4.89 (0.01)	2049.0 (129.6)	$8.98 \times 10^4$	34.0 (2.8)	$5.32 \times 10^3$
L26-16	4/40	4.89 (0.03)	14266.5 (1857.1)	$4.83 \times 10^5$	24.3 (4.5)	$2.86 \times 10^4$
L26-18	2/20	4.84 (0.02)	2374.9 (31.8)	$7.88 \times 10^4$	23.2 (0.5)	$4.67 \times 10^3$
L26-17	2/20	4.87 (0.03)	2217.6 (47.7)	$8.98 \times 10^4$	30.5 (0.9)	$5.32 \times 10^3$
L26-16	2/20	4.90 (0.04)	17301.2 (3338.0)	$4.83 \times 10^5$	18.5 (5.4)	$2.86 \times 10^4$

Each of the L26 lysimeter sediments, which were collected from sediments located several centimeters below the filter-paper radionuclide source, contained  $\sim 200,000$  Bq kg<sup>-1</sup> of  $^{133}\text{Ba}$ . This

indicates that  $^{133}\text{Ba}$  was effectively mobilized away from the filter-paper source. Although no  $^{133}\text{Ba}$  was detected in the L26 lysimeter effluent,<sup>12</sup> the  $K_d$  values determined in this work (24.9–30.7 mL g<sup>-1</sup>, Table 5) indicate that Ba was not strongly adsorbed to the SRS sediments. These  $K_d$  values are approximately 10-times larger than those determined in a seven-day laboratory study for  $^{85}\text{Sr}$ ,<sup>14</sup> which is expected to exhibit similar chemistry to Ba.

The  $^{152}\text{Eu}$   $K_d$  values for the L26 lysimeter sediments ranged from 2180 to 7590 mL g<sup>-1</sup> (Table 6), indicating strong sorption to the SRS sediments. These  $K_d$  values are significantly larger than those measured for  $^{60}\text{Co}$  or  $^{133}\text{Ba}$  (Tables 4 and 5, respectively). However, the  $^{152}\text{Eu}$   $K_d$  values (Table 6) are similar (within error) to the  $^{137}\text{Cs}$   $K_d$  values (Table 2) measured for the same lysimeter sediments. This finding is surprising, given that stronger sorption is expected for trivalent metal cations (e.g.,  $\text{Eu}^{3+}$ ) than for monovalent metal cations (e.g.,  $\text{Cs}^+$ ). Furthermore, although the  $^{152}\text{Eu}$   $K_d$  values determined here are approximately 4–10 times larger than those reported in a seven-day laboratory sorption study,<sup>20</sup> which is an indication that Eu sorption increases with increasing sediment contact time, the influence of contact time on sorption is less pronounced for Eu than for Cs, for which “aging” yields  $^{137}\text{Cs}$   $K_d$  values 1000-times greater than those measured in short-term experiments. The similar  $K_d$  values measured for  $^{137}\text{Cs}$  and  $^{152}\text{Eu}$ , despite large differences in the charge densities of these two metal cations, combined with the greater “aging” effect for Cs sorption, suggests that different mechanisms are responsible for Eu and Cs sorption to SRS sediments.

Table 5: Average  $^{133}\text{Ba}$  extraction activities, total activities, and  $K_d$  values for lysimeter L26. Numbers in parentheses are the standard deviation to the means.

Sample name	Solid/Solution ratio (kg/L)	pH	Extract activity (Bq/L)	Total activity (Bq/kg)	$K_d$ (mL/g)	Maximum detectable $K_d$ (mL/g)
L26-18	4/40	4.88 (0.03)	5368.7 (415.5)	$2.17 \times 10^5$	30.5 (3.2)	$2.30 \times 10^4$
L26-17	4/40	4.89 (0.01)	5466.8 (234.7)	$2.12 \times 10^5$	28.9 (1.7)	$2.25 \times 10^4$
L26-16	4/40	4.89 (0.03)	5192.5 (769.6)	$2.08 \times 10^5$	30.7 (6.1)	$2.21 \times 10^4$
L26-18	2/20	4.84 (0.02)	6188.3 (298.1)	$2.17 \times 10^5$	25.1 (1.8)	$2.30 \times 10^4$
L26-17	2/20	4.87 (0.03)	5546.0 (33.1)	$2.12 \times 10^5$	28.3 (0.2)	$2.25 \times 10^4$
L26-16	2/20	4.90 (0.04)	6017.7 (681.3)	$2.08 \times 10^5$	24.9 (3.9)	$2.21 \times 10^4$

Table 6: Average  $^{152}\text{Eu}$  extraction activities, total activities, and  $K_d$  values for lysimeter L26. Numbers in parentheses are the standard deviation to the means, and “-” activities are below detection limits.

Sample name	Solid/Solute ion ratio (kg/L)	pH	Extract activity (Bq/L)	Total activity (Bq/kg)	$K_d$ (mL/g)	Maximum detectable $K_d$ (mL/g)
L26-18	4/40	4.88 (0.03)	-	$5.78 \times 10^2$	-	$1.94 \times 10^1$
L26-17	4/40	4.89 (0.01)	38.5 (19.7)	$2.47 \times 10^5$	7,590 (3,660)	$8.28 \times 10^3$
L26-16	4/40	4.89 (0.03)	992.2 (162.3)	$3.10 \times 10^6$	3,170 (523)	$1.04 \times 10^5$
L26-18	2/20	4.84 (0.02)	-	$5.78 \times 10^2$	-	$1.94 \times 10^1$
L26-17	2/20	4.87 (0.03)	78.8 (12.0)	$2.47 \times 10^5$	3,160 (481)	$8.28 \times 10^3$
L26-16	2/20	4.90 (0.04)	1417.0 (62.1)	$3.10 \times 10^6$	2,180 (96)	$1.04 \times 10^5$

## 5. Summary

Overall, this study demonstrates the potential for aging, wherein the affinity of  $^{152}\text{Eu}$  and  $^{137}\text{Cs}$  for sediments from the SRS increases over time. The greater  $^{137}\text{Cs}$   $K_d$  value for the M2 and L26 sediments compared with reported laboratory studies indicate that increased contact time with sediments increases Cs sorption. A similar aging process was observed for  $^{152}\text{Eu}$  when the  $K_d$  values measured here for the L26 lysimeter samples are compared with values measured from short-term laboratory studies. No significant aging occurs for  $^{60}\text{Co}$  based on the results from this work. Further studies are needed to determine if aging increases  $^{133}\text{Ba}$  sorption.

Using data from all samples (reported in Appendix A, Table A.2), the average  $K_d$  values and standard deviations for each isotope evaluated in this study are:

- $^{60}\text{Co}$ :  $29.0 \pm 9.2$  L/kg (n = 15)
- $^{133}\text{Ba}$ :  $28.5 \pm 3.7$  L/kg (n = 15)
- $^{137}\text{Cs}$ :  $2,242.8 \pm 375.2$  L/kg (n = 11)
- $^{152}\text{Eu}$ :  $4,293 \pm 2,896$  L/kg (n = 10)

## 6. Appendix

Table A.1: Measured source concentrations of each isotope determined in Clemson Environmental Radiochemistry Laboratory. Sample M2-1305 was not analyzed due to insufficient soil mass available for the analysis.

Isotope	Sample Name			
	L26-18	L26-17	L26-16	M2-1309
<sup>137</sup> Cs	1.53E+04	2.63E+05	1.99E+06	3.63E+03
<sup>60</sup> Co	7.88E+04	8.98E+04	4.83E+05	1.49E+01
<sup>133</sup> Ba	2.17E+05	2.12E+05	2.08E+05	5.53E+00
<sup>152</sup> Eu	5.78E+02	2.47E+05	3.10E+06	1.38E+02

Table A.2: K<sub>d</sub> values determined from individual experiments as well as average and standard deviations of all samples above detection limits.

Sample ID*	<sup>60</sup> Co K <sub>d</sub> (L/kg)	<sup>133</sup> Ba K <sub>d</sub> (L/kg)	<sup>137</sup> Cs K <sub>d</sub> (L/kg)	<sup>152</sup> Eu K <sub>d</sub> (L/kg)
L26-18-4/40 A	30.0	27.5	BLD	BLD
L26-18-4/40 B	31.5	30.2	BLD	BLD
L26-18-4/40 C	54.8	33.9	BLD	BLD
L26-17-4/40 A	33.6	27.2	2028	4,089
L26-17-4/40 B	31.4	29.1	2180	7,286
L26-17-4/40 C	36.9	30.6	2765	11,389
L26-16-4/40 A	29.1	37.0	2907	3,709
L26-16-4/40 B	23.6	30.3	2491	3,124
L26-16-4/40 C	20.1	24.9	2321	2,666
M2-1309 4/40 A	-	-	BLD	-
M2-1309 4/40 B	-	-	BLD	-
M2-1305 4/40 A	-	-	BLD	-
M2-1305 4/40 B	-	-	2051	-
L26-18-2/20 A	22.8	23.8	BLD	BLD
L26-18-2/20 B	23.6	26.3	BLD	BLD
L26-17-2/20 A	29.9	28.2	1895	2,818
L26-17-2/20 B	31.1	28.5	2241	3,498
L26-16-2/20 A	14.7	22.1	1598	2,109
L26-16-2/20 B	22.4	27.6	2194	2,244
<b>Average</b>	29.0	28.5	2242.8	4,293
<b>Standard Deviation</b>	9.2	3.7	375.2	2,896

-: insufficient concentration of isotope within soil for K<sub>d</sub> determination

BLD: aqueous phase concentration was below detection limit

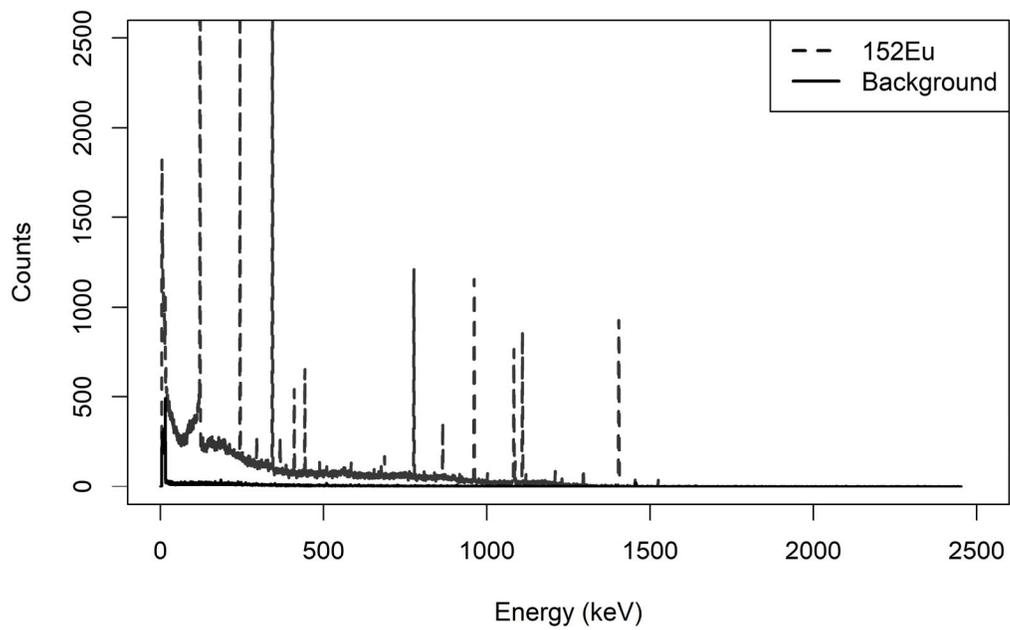


Figure A1: Gamma spectrum of the NIST-certified  $^{152}\text{Eu}$  standard.

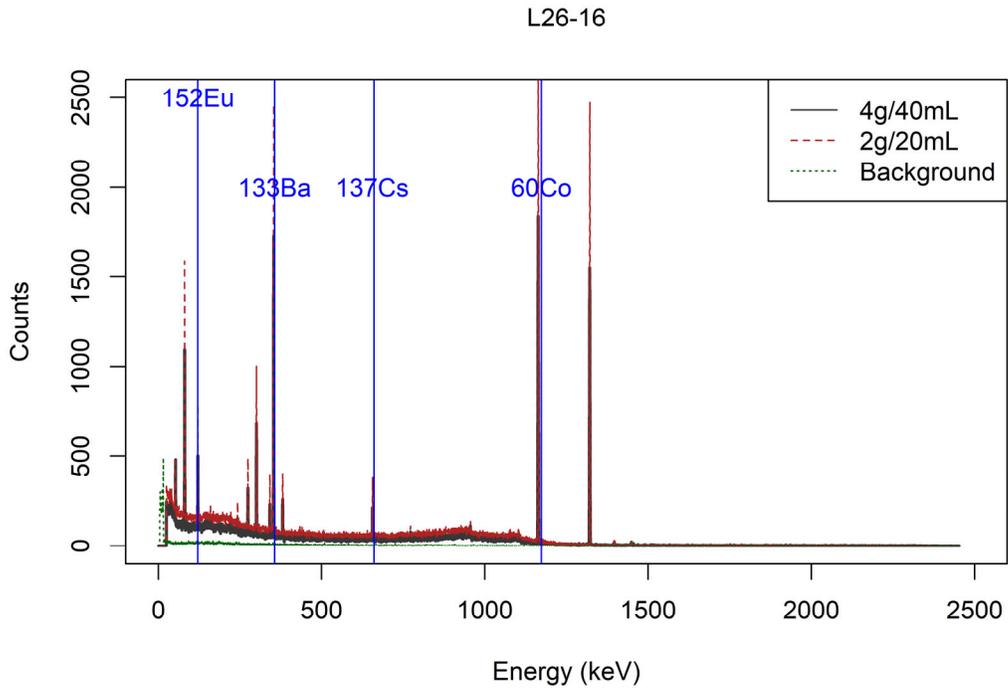


Figure A2: Gamma spectra of the L26-16 extract samples.

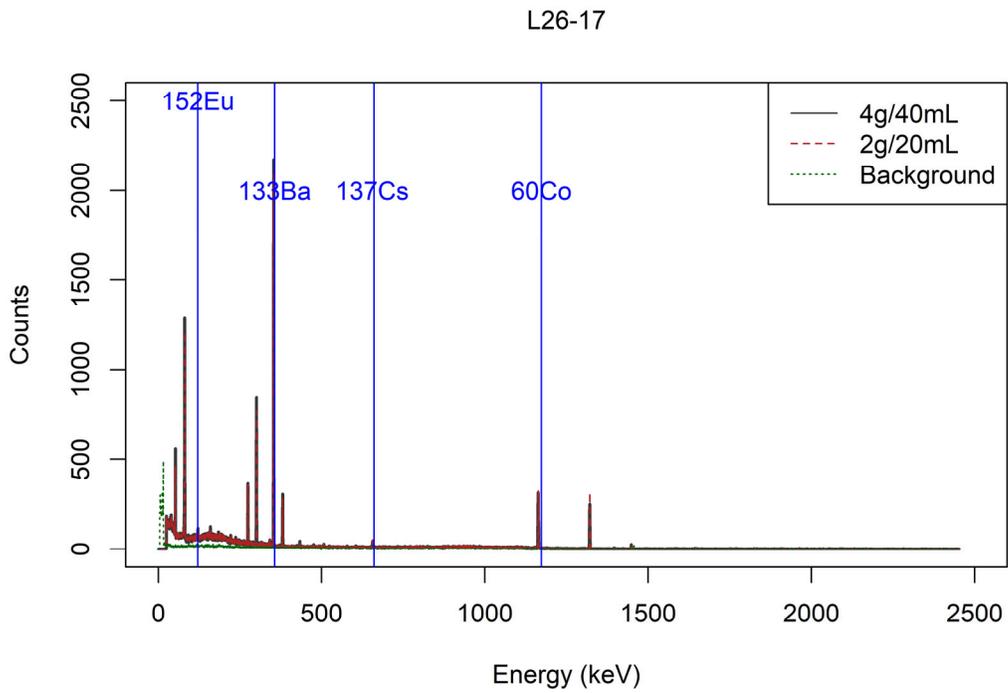


Figure A3: Gamma spectra of the L26-17 extract samples.

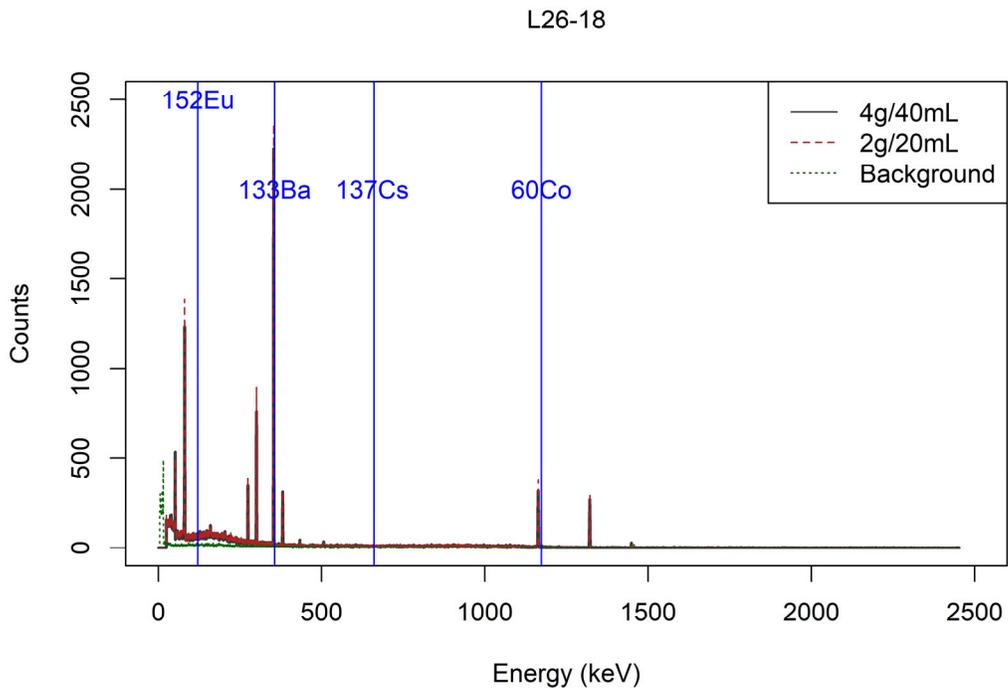


Figure A4: Gamma spectra of the L26-18 extract samples.

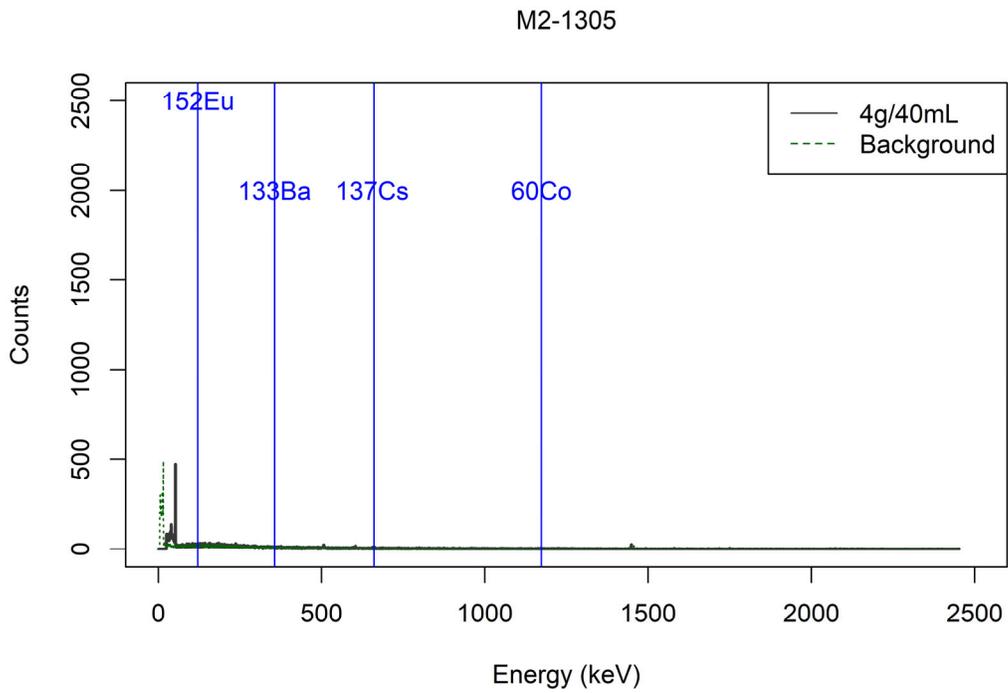


Figure A5: Gamma spectrum of the M2-1305 4/40 extract sample.

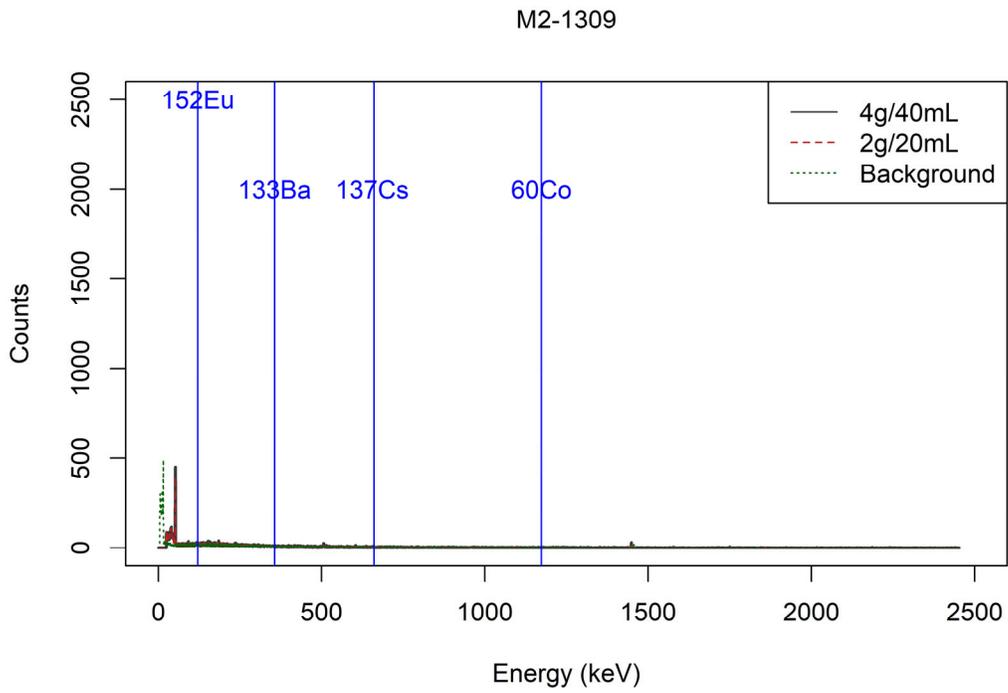


Figure A6: Gamma spectra of the M2-1309 extract samples.



Figure A6: Photograph of the dried L26 and M2 lysimeter sediments as received from the SRS.

## 7. Literature Cited

- (1) Lee, W. E.; Ojovan, M. I.; Stennett, M. C.; Hyatt, N. C. Immobilisation of Radioactive Waste in Glasses, Glass Composite Materials and Ceramics. *Adv. Appl. Ceram.* **2006**, *105* (1), 3–12.
- (2) Ojovan, M. I.; Lee, W. E. Glassy Wasteforms for Nuclear Waste Immobilization. *Metall. Mater. Trans. A* **2011**, *42* (4), 837–851.
- (3) Wicks, G. G. US Field Testing Programs and Results. *J. Nucl. Mater.* **2001**, *298* (1), 78–85.
- (4) Curti, E.; Crovisier, J. L.; Morvan, G.; Karpoff, A. M. Long-Term Corrosion of Two Nuclear Waste Reference Glasses (MW and SON68): A Kinetic and Mineral Alteration Study. *Appl. Geochem.* **2006**, *21* (7), 1152–1168.
- (5) Thien, B.; Godon, N.; Hubert, F.; Angéli, F.; Gin, S.; Ayrat, A. Structural Identification of a Trioctahedral Smectite Formed by the Aqueous Alteration of a Nuclear Glass. *Appl. Clay Sci.* **2010**, *49* (3), 135–141.
- (6) Hand, R. J. The Ballidon Glass Burial Experiment—35 Years On. *Glass Technol.* **2005**, *46* (6), 237–242.
- (7) McCarthy, G. J.; White, W. B.; Roy, R.; Scheetz, B. E.; Komarneni, S.; Smith, D. K.; Roy, D. M. Interactions between Nuclear Waste and Surrounding Rock. *Nature* **1978**, *273* (5659), 216–217.
- (8) Curti, E.; Dähn, R.; Farges, F.; Vespa, M. Na, Mg, Ni and Cs Distribution and Speciation after Long-Term Alteration of a Simulated Nuclear Waste Glass: A Micro-XAS/XRF/XRD and Wet Chemical Study. *Geochim. Cosmochim. Acta* **2009**, *73* (8), 2283–2298.
- (9) Jantzen, C. M.; Kaplan, D. I.; Bibler, N. E.; Peeler, D. K.; John Plodinec, M. Performance of a Buried Radioactive High Level Waste (HLW) Glass after 24 Years. *J. Nucl. Mater.* **2008**, *378* (3), 244–256.
- (10) Guittonneau, C.; Gin, S.; Godon, N.; Mestre, J. P.; Dugne, O.; Allegri, P. A 25-Year Laboratory Experiment on French SON68 Nuclear Glass Leached in a Granitic Environment – First Investigations. *J. Nucl. Mater.* **2011**, *408* (1), 73–89.
- (11) Roberts, K.; Kaplan, D.; Bagwell, L.; Powell, B.; Almond, P.; Emerson, H.; Hixon, A.; Jablonski, J.; Buchanan, C.; Waterhouse, T. *SRNL Radionuclide Field Lysimeter Experiment: Baseline Construction and Implementation*; SRNL-STI-2012-00603; Savannah River National Laboratory; Savannah River Nuclear Solutions, LLC: Aiken, SC, USA, 2012; p SRNL-STI-2012-00603, 1053691.
- (12) Peruski, K.; Pope, R.; Maloubier, M.; Powell, B. A. *Determination of Constituent Concentrations in Field Lysimeter Effluents*; SRRA021685SR; Clemson University, 2017.
- (13) Currie, L. A. Limits for Qualitative Detection and Quantitative Determination. Application to Radiochemistry. *Anal. Chem.* **1968**, *40* (3), 586–593.
- (14) Grogan, K. P.; Fjeld, R. A.; Kaplan, D.; DeVol, T. A.; Coates, J. T. Distributions of Radionuclide Sorption Coefficients (Kd) in Sub-Surface Sediments and the Implications for Transport Calculations. *J. Environ. Radioact.* **2010**, *101* (10), 847–853.
- (15) Wampler, J. M.; Krogstad, E. J.; Elliott, W. C.; Kahn, B.; Kaplan, D. I. Long-Term Selective Retention of Natural Cs and Rb by Highly Weathered Coastal Plain Soils. *Environ. Sci. Technol.* **2012**, *46* (7), 3837–3843.

- (16) Zaunbrecher, L. K.; Elliott, W. C.; Wampler, J. M.; Perdrial, N.; Kaplan, D. I. Enrichment of Cesium and Rubidium in Weathered Micaceous Materials at the Savannah River Site, South Carolina. *Environ. Sci. Technol.* **2015**, *49* (7), 4226–4234.
- (17) Zaunbrecher, L. K.; Cygan, R. T.; Elliott, W. C. Molecular Models of Cesium and Rubidium Adsorption on Weathered Micaceous Minerals. *J. Phys. Chem. A* **2015**, *119* (22), 5691–5700.
- (18) Kwong-Moses, D. S.; Elliott, W. C.; Wampler, J. M.; Powell, B. A.; Avant, D. M. Sorption and Desorption of Radiocesium by Muscovite Separated from the Georgia Kaolin. *J. Environ. Radioact.* **2020**, *211*, 106074.
- (19) Goto, M.; Rosson, R.; Elliott, W. C.; Wampler, J. M.; Serkiz, S.; Kahn, B. Interactions of Radioactive and Stable Cesium with Hydroxy-Interlayered Vermiculite Grains in Soils of the Savannah River Site, South Carolina, USA. *Clays Clay Miner.* **2014**, *62* (3), 161–173.
- (20) Kaplan, D. I.; Serkiz, S. M.; Allison, J. D. Europium Sorption to Sediments in the Presence of Natural Organic Matter: A Laboratory and Modeling Study. *Appl. Geochem.* **2010**, *25* (2), 224–232.