SRNS-STI-2008-00445, REVISION 1

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Carbonate Distribution
Coefficient (K_d), Desorption,
Anion Exchange, Sediments,
Concrete

Retention:
Permanent

CARBON-14 GEOCHEMISTRY AT THE SAVANNAH RIVER SITE

Kimberly A. Roberts
Daniel I. Kaplan

5/10/2013

Savannah River National Laboratory
Savannah River Nuclear Solutions
Savannah River Site
Aiken, SC 29808
Prepared for the U.S. Department of Energy Under
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REVIEWS AND APPROVALS

Kimberly A. Roberts, Co-author, Radiological Performance Assessment Date

Daniel I. Kaplan, Co-author, Environmental Sciences Date

Morgana T. Whiteside, Peer Reviewer, Analytical Technical Support Date

David A. Crowley, Manager, Radiological Performance Assessment Date

R. S. Aylward, Manager, Environmental Management Date

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LIST OF ACRONYMS

cpm	Counts per minute
K_d	Distribution Coefficient
SRS	Savannah River Site
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
OBG	Old Burial Ground
MWMF	Mixed Waste Management Facility
LLRDWF	Low-level Radioactive Disposal Waste Facility
PA	Performance Assessment

1.0 EXECUTIVE SUMMARY

Carbon-14 is among the key radionuclides driving risk at the E-Area Low-Level Waste Disposal Facility on the Savannah River Site (SRS). Much of this calculated risk is believed to be the result of having to make conservative assumptions in risk calculations because of the lack of site-specific data. The original geochemical data package (Kaplan 2006) recommended that performance assessments and composite analyses for the SRS assume that ^{14}C did not sorbed to sediments or cementitious materials, i.e., that C-14 K_d value (solid:liquid concentration ratio) be set to 0 mL/g (Kaplan 2006). This recommendation was based primarily on the fact that no site-specific experimental work was available and the assumption that the interaction of anionic ^{14}C (as CO_2^{2-}) with similarly charged sediments or cementitious materials would be minimal. When used in reactive transport equations, the 0 mL/g K_d value results in ^{14}C not interacting with the solid phase and moving quickly through the porous media at the same rate as water. The objective of this study was to quantify and understand how aqueous ^{14}C, as dissolved carbonate, sorbs to and desorbs from SRS sediments and cementitious materials.

Laboratory studies measuring the sorption of ^{14}C, added as a carbonate, showed unequivocally that ^{14}C-carbonate K_d values were not equal to 0 mL/g for any of the solid phases tested, but they required several months to come to steady state. After six months of contact, the apparent K_d values for a clayey sediment was 3,000 mL/g, for a sandy sediment was 10 mL/g, for a 36-year-old concrete was 30,000 mL/g, and for a reducing grout was 40 mL/g. Furthermore, it was demonstrated that (ad)sorption rates were appreciably faster than desorption rates, indicating that a kinetic sorption model, as opposed to the steady-state K_d model, may be a more accurate description of the ^{14}C-carbonate sorption process. A second study demonstrated that the ^{14}C-carbonate sorbed very strongly onto the various materials and could not be desorbed by anion exchanged with high concentrations of carbonate or nitrate. High phosphate concentrations were able to desorb ^{14}C-carbonate from the 36-year-old concrete sample, but not the clayey sediment sample. Together these geochemistry studies support the use of non-zero K_d values in risk calculations on the SRS.

For performance assessment (PA) calculations, ^{14}C would be moving with the groundwater, remaining in contact with sediment for days, not months. Therefore for purposes of SRS risk calculations, it is appropriate to select sorption values after a couple days of contact, departing from the traditional definition that states K_d values reflect the system under steady state conditions. Such an “apparent K_d value,” would be expected to provide a better (and more conservative) estimate of what to expect under SRS PA conditions. Based on these results, recommended apparent K_d values for use in the PA are 1 mL/g for sandy sediments and 30 mL/g for clayey sediments.

This document is a revision of a document issued on 12/09/2008 (Roberts and Kaplan 2008). This revision includes recommended “apparent K_d values” based on contact times of a couple days (as well as some editorial changes).

2.0 INTRODUCTION

Carbon-14 ($t_{1/2}$= 5730 years) was produced at the Savannah River Site (SRS) from 1954 to 1989 by the ^{17}O (n, α) ^{14}C reaction. Areas on the SRS at which ^{14}C was found are the Old Burial Ground (OBG), the Mixed Waste Management Facility (MWMF), and the E-Area Low-level Radioactive Waste Disposal Facility (LLRWDF). Estimates of the total ^{14}C released or placed in the ground as low-level waste are as much as 6600 Ci (McIntyre, 1988; Hiergesell et al., 2008).

Given the large quantity of ^{14}C at the SRS, it is important to develop an accurate conceptual biogeochemical model as well as to quantify the important processes influencing ^{14}C fate and transport in the environment. A majority of the ^{14}C in the LLRWDF is believed to be associated with resins, existing as loose entities or contained within stainless steel containment vessels (from the K- and L- Disassembly Basin Facility), used to maintain low dissolved salts and radionuclide concentrations in spent fuel basin waters.

Carbonate chemistry is complex because under field conditions it can exist as a solid, liquid, and/or gas and its speciation is highly pH dependent. Figure 1 shows carbon speciation as a function of pH where $H_2CO_3^0$ and HCO_3^- dominate under most groundwater pH conditions, and CO_3^{2-} is the primary species only under very alkaline conditions, pH values >10, such as cementitious environments. It is anticipated that there will be negligible amounts of ^{14}C existing as organic moieties in the aqueous phase of the low-level waste environment because much of the ^{14}C originates from inorganic carbonate adsorbed to anion exchange resins from the K and L Disassembly Basin Facility and there is relatively little organic carbon, such as fulvic and humic acids, in the SRS subsurface groundwater.

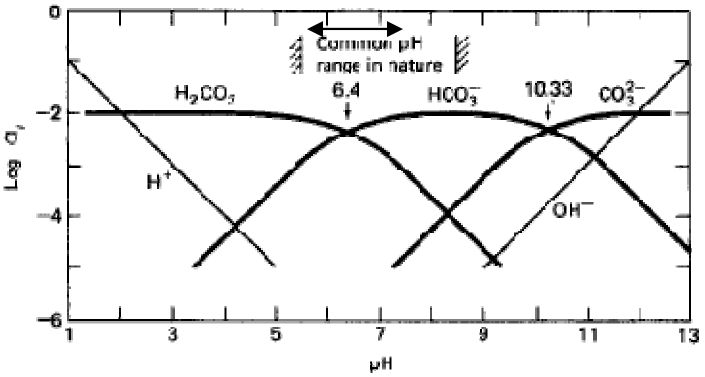

Figure 1. Bjerrum plot of carbonate species at $CO_2 = 10^{-2}$ and T= 25°C (from Drever, 1997). The expected pH range for solution in contact with cementitious materials is pH 10 to 13.

Currently, SRS models use an equilibrium isotherm based K_d (sediment-water partitioning coefficient) value of 0 mL/g indicating that there is no sorption of or interaction between ^{14}C and subsurface soils (Kaplan 2006). Here local sorption and desorption rates are assumed to be infinite thus resulting in local phasic equilibrium at all time scales. This is a conservative approach and one that is used because studies using site-specific materials have not been undertaken to measure more accurate values. This low K_d value is based on the assumption that ^{14}C exists as a carbonate, thereby possessing a negative charge and being repulsed from SRS sediments and cementitious materials, which also have negative charges. Chemical behavior of ^{14}C would depend greatly on the disposal location and the geochemistry of its immediate surroundings, *i.e.,* background sediment, stainless steel, and cementitious materials. In turn, these varying background materials would influence the pH and thus the dominant carbonate species.

Much is known about carbonate chemistry in alkaline environments, but much less is known about it under slightly acidic conditions, as exist in natural SRS sediments (Reeder 1983). This is due to carbonate minerals existing only in alkaline conditions. The sorptive behavior of ^{14}C, primarily via adsorption, is generally of much less widespread interest than understanding natural stable ^{12}C-carbonates. McIntyre (1988) measured ^{14}C, as a carbonate, transient K_d values on SRS sediment of 2 mL/g after 7 hours and 55 mL/g after 72 hours. Table 1 is a compilation of ^{14}C sorption data for different solids by Allard et al. (1981). The large K_d values after 1 week for the concrete and cement paste likely represent sorption via coprecipitation as a solid carbonate phase.

Table 1. K_d (mL/g) data for ^{14}C on different solids as a function of time (from Allard et. al, 1981) where h= hour, d = day, w = week and m = month.

Solid	*0.5h*	*2h*	*6h*	*24h*	*3d*	*1w*	*5w*	*6m*
Bentonite/quartz					2.8	8.6	7.6	7.8
Sandy moraine	1	0.2	0.7	0.5	0.8	1.1	2.6	2.2
Clayish moraine	1.9	0.7	1.3	1.4	1.3	2.0	3.0	2.3
Calcite	1.0	1.0	1.5	1.7	3.7	3.5	9.0	83
Concrete					5.3	1600	$>10^4$	
Cement paste					7.4	1600	$>10^4$	

The process of desorption of ^{14}C is also of interest because a hysteresis effect is commonly reported for radionuclides that sorb via precipitation or coprecipitation (Krupka et al. 1999). Hysteresis is the process when (ad)sorption and desorption rates of solutes to solids are markedly different. The K_d construct assumes (ad)sorption and desorption rates are identical and large. There are many examples in the literature of when desorption is slower than (ad)sorption rates, especially when precipitation or coprecipitation of the solute has occurred.

Kaplan and Coffey (2002) found that the desorption K_d for ^{14}C from spent resin was 240 mL/g in acid-rain leachate (lower pH) and 140 mL/g in cement leachate (higher pH). This data suggests that not only is the solid phase important (in this case resin) but also the pH of the system in understanding K_d values.

The existence of non-zero K_d values in the literature provides an impetus for measuring SRS site-specific values. Thus, the objectives of this study were to:

1. measure $^{14}CO_3^{2-}/H^{14}CO_3^{-}/H_2CO_3^0$ (henceforth referred to as carbonate) sorption parameters, K_d or solubility values, on SRS sediments and cementitious materials applicable for use in SRS performance assessments and composite analyses;
2. determine the sorption kinetics of ^{14}C-carbonate onto these surfaces to evaluate whether the sorption reaction is kinetically hindered, compromising the application of the K_d construct in reactive transport modeling; and
3. determine how strongly ^{14}C-carbonate is retained by geo-sorbents by adding varying concentrations of competing anions. The competitive anions will have varying valences and ionic radii.

3.0 MATERIALS AND METHODS

3.1 MATERIALS

Detailed experimental procedures are documented in Appendix A. Briefly, 1g of sediment or 0.1 g of cementitious material was combined with 10 mL of SRS groundwater (collected from near PAR Pond). Characterization of the two sediments is presented in Table 2. There were two types of cementitious materials. One was an aged cementitious material recovered from the base pad of a non-rad tank located in P-Area of the SRS that was poured in 1972 and had been exposed to the natural elements since then. An internal portion of the core, a portion that was not in contact with the air or the underlying soil, was taken for use in this study. The sample was crushed, passed through a mill, and then the <1-mm fraction was used in this study. The second cementitious sample was a reducing grout, similar to those that may be used in tank closure. This sample was prepared by Christine Langton (SRNL), permitted to cure for 1 month, crushed, milled, and then passed through a 1-mm sieve. The <1-mm sieved fraction was used in these tests. Some properties of these materials are presented in Table 3 and the formulation of the reducing grout is presented in Table 4.

3.2 METHODS FOR THE (AD)SORPTION EXPERIMENT

A ^{14}C-carbonate spike solution (^{14}C-carbonate as sodium carbonate in 0.001M NaOH) was added to create a suspension with a final specific activity of 0.0017 µCi/L ^{14}C. The resulting suspension was mixed by hand twice a day for 1.7, 19, and 24.6 hours, 4.8 and 13 days, and 6.3 months. The solids were separated from the liquids by passing the liquids through a 0.1-µm syringe filter and analyzed for ^{14}C concentrations by liquid scintillation counting. No acid preservative was added to the sample because of the anionic character of the ^{14}C-carbonate.

The K_d value was calculated as follows:

$$K_d = (\text{cpm}_{\text{nosolid controls}} - \text{cpm}_{\text{in solution}})/(\text{cpm}_{\text{in solution}} *(\text{particle weight (g)/volume(L)})) \qquad [1]$$

where cpm represents counts per minute.

3.3 METHODS FOR THE DESORPTION EXPERIMENT

^{14}C desorption experiments were conducted with the clayey sediment and cementitious materials that had been equilibrated with ^{14}C-carbonate for four days. Approximately 8 mL of 0.1M solutions of $NaNO_3$, Na_2CO_3, or $Na_2HPO_4*7H_2O$ were added to the solids in the centrifuge tubes. For two weeks these tubes were then mixed twice a day by shaking by hand. The solid and aqueous phases were then separated and the aqueous phase was passed through a 0.1-µm filter and analyzed for ^{14}C by liquid scintillation.

Table 2. Sediment characterization.

	Units	Red Subsurface Clayey Sediment	Yellow Subsurface Sandy Sediment	Analytical Method
Sand / Silt / Clay	Wt-%	13 / 30 / 58	1 / 2 / 97	Pipette and sieve method (Miller and Miller, 1987)
Surface Area	m^2/g	15.31	2.4	B.E.T. (Brunauer, Emmett and Teller, 1938)
pH		4.55	5.1	1:1 sediment:water
Organic Matter	Wt-%	<0.02	<0.02	Combustion (Allen, 1986, pp. 15-16)
Extractable Fe	Wt-%	1.50	0.72	Citrate-dithionate method (Sparks 1996, pp. 647-648)
CEC[a]	$cmol_+/kg$	1.09	NA	Unbuffered Salt Extraction Method (Sparks 1996, pp. 1218-1220)
AEC[a]	cmol-/kg	1.58	0.06	Unbuffered Salt Extraction Method (Sparks 1996, pp. 1218-1220)

[a] CEC = cation exchange capacity; AEC = anion exchange capacity

Table 3. Characterization of the cementitious materials used in studies.

Cementitious Materials	*BET surface Area (m^2/g)*	*pH (1:1 water:cement)*	*Eh (mV; 1:1 water:cement)*
Reducing Grout	7.11 ± 0.02	11.16	36
36-yr- old Concrete	5.88 ± 0.02	11.99	347

Table 4. Reducing grout formulation. [a]

Ingredient	*Amount Added*
Slag	210 lb/yd^3
Water	60 gallons/yd^3
Portland cement	75 lb/yd^3
Fly ash	375 lb/yd^3
sand	2300 lb/yd^3
KelcoCrete	90 oz/yd^3
Sodium thiosulfate	2.1 lb/yd^3

[a] Reducing grout sample prepared by Chrisine Langton (SRNL) and identified as sample OPDEXE-X-P-O-BS.

4.0 RESULTS AND DISCUSSION OF GEOCHEMISTRY EXPERIMENTS

4.1 (AD)SORPTION EXPERIMENT

Sorption of ^{14}C-carbonate on SRS subsurface clay sediment increased from the initial (t = 0.07 d) to second contact time point (t = 0.8 d) (Figure 2). There was no statistical difference in ^{14}C-carbonate sorption between the next four time points (t = 0.8 – 13.1 d), but a substantial increase in sorption was measured between 13.1 days and 189.2 days (6.3 months), at which time nearly 95% sorption was measured. ^{14}C-carbonate sorption to the sand subsurface sediment (Figure 3) was more erratic between 0.07 to 13.1 days, but a significant increase was measured between 13.1 and 189.2 days, when 40% of the ^{14}C-carbonate was sorbed. The respective K_d values for clay and sand at 189.2 days (6.3 months) were 372 mL/g and 8.64 mL/g. If these values are normalized by surface area (Table 2), the resulting K_d values are 24.3 mL/m^2 for clay and 3.6 mLl/m^2 for sand. Therefore the surface area correction reduced the difference between the K_d values; clayey sediment had a weight-normalized K_d value and a surface-area normalized K_d value that was 43 and 7 times greater than that for the sandy sediment, respectively.

The sorption of ^{14}C-carbonate to 36-year-old concrete (Figure 4) increased during the first day and then remained constant for the ensuing two weeks. Between the 13.1 and 189.2 day measurements, nearly all the remaining ^{14}C-carbonate was sorbed. The trend of ^{14}C-carbonate sorption to the 36-year-old concrete was similar to that for the clayey sediment (Figure 2). ^{14}C-carbonate sorption to the reducing grout (Figure 5) followed a similar trend as observed with the 36-year-old concrete, with a significant increase in sorption measured between 13.1 and 6.3 months. However, only 25% of the added ^{14}C-carbonate sorbed to the reducing grout (Figure 5), which was the lowest percentage for all of the solids tested here.

Solids concentrations for the cementitious solids were a factor of 10 lower than for sediments because it was anticipated the former would have greater sorption affinities for ^{14}C-carbonate. The reason for the lower sorption of the reducing grout is not known. The major difference between reducing grout and the 36-year-old concrete is the presence of a reducing agent, slag, in the former. It is not clear why slag would cause carbonate sorption to decrease, given that the two pH levels were nearly identical at pH 11 (Table 3). Yet, under our experimental conditions (i.e., not 1:1 water: solid as in Table 3), there was a significant difference in pH with values of 8-9 for cement and pH 5-6 for slag-containing cement. While the slag is not expected to reduce carbonate, perhaps the presence of the slag anions and cations influenced carbonate sorption.

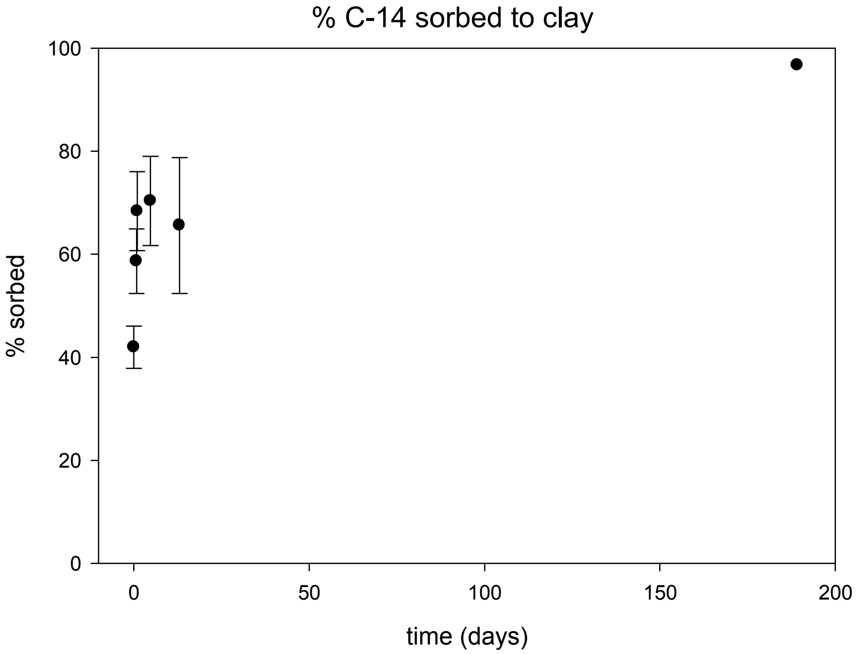

Figure 2. Percent of ^{14}C, added as $Na_2{}^{14}CO_3$, sorbed to clay particles as a function of time with a particle concentration of 83.3 mg/L. Each data point represents the average of replicate measurements (except for time = 180 days, n = 1) and the error bar represents propagated counting uncertainty.

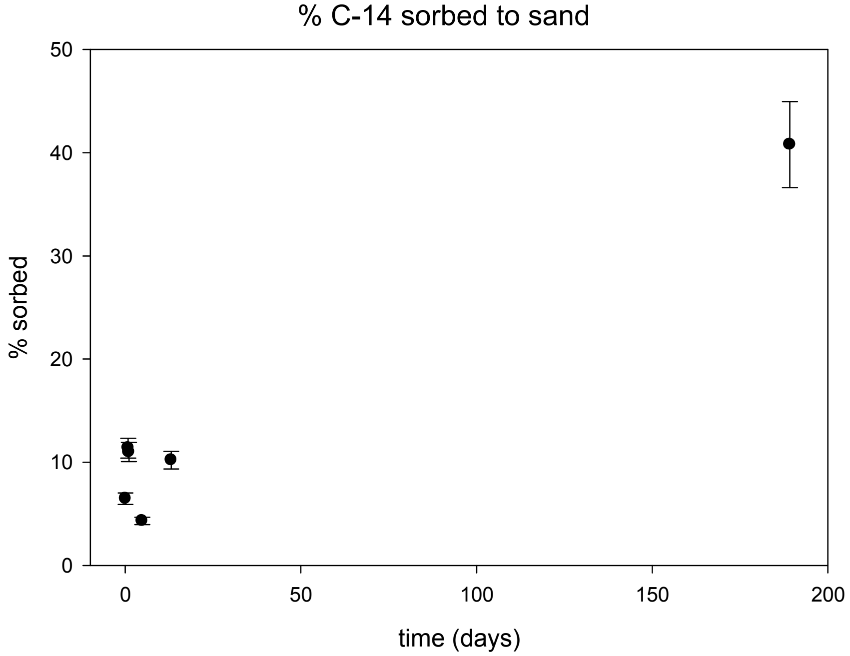

Figure 3. Percent of ^{14}C, added as $Na_2{}^{14}CO_3$, sorbed to sand particles as a function of time with a particle concentration of 83.3 mg/L. Each data point represents the average of replicate measurements and the error bar is propagated counting uncertainty.

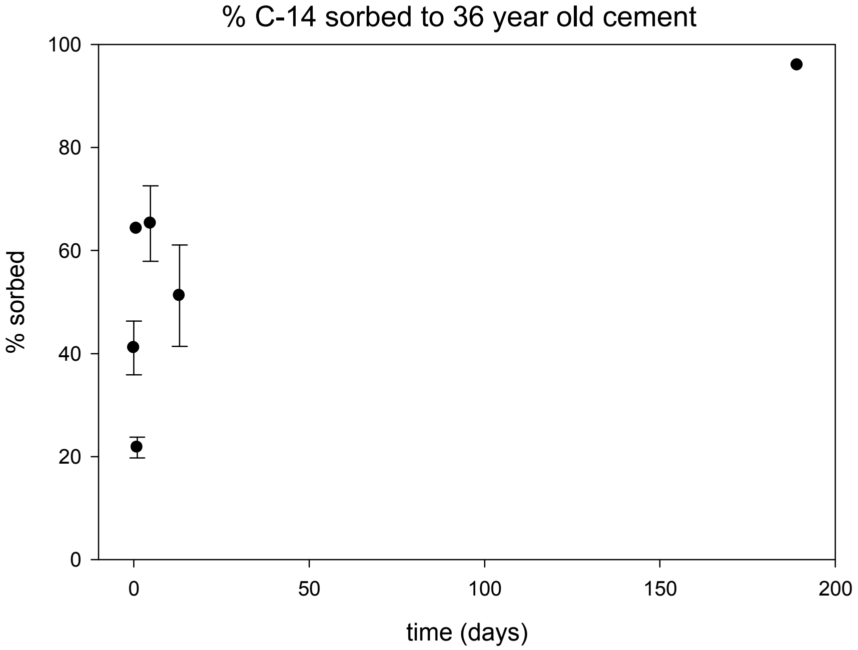

Figure 4. Percent of ^{14}C, added as $Na_2{}^{14}CO_3$, sorbed to 36-year-old concrete as a function of time with a particle concentration of 8.3 mg/L. Each data point represents the average of replicate measurements (except for time = 180 days, n = 1) and the error bar is propagated counting uncertainty.

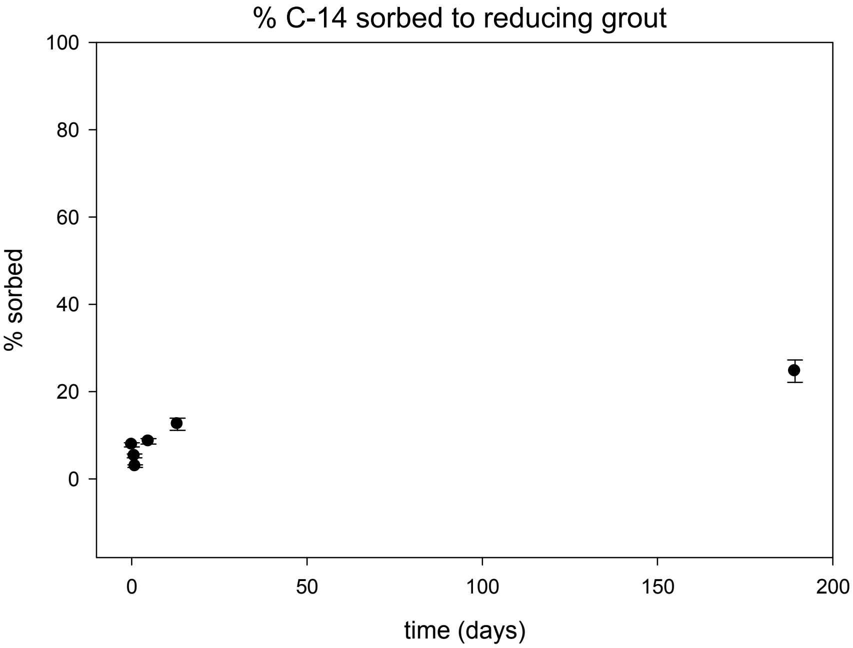

Figure 5. Percent of ^{14}C, added as $Na_2{}^{14}CO_3$, sorbed to reducing grout particles as a function of time with a particle concentration of 8.3 mg/L. Each data point represents the average of replicate measurements and the error bar is the propagated counting uncertainty.

These results can also be presented in the form of K_d values (Table 5). The data shows roughly the same trends as Figure 2 through Figure 5 though the propagated errors in the K_d's indicate less of a significance, especially in the first 5 data points (up to 13.1d). As stated above, the system was never demonstrated to have achieved complete steady state (This is demonstrated by measuring no change in aqueous^{14}C concentrations (or K_d values) for the last two or three contact durations), even after 6.3 months of equilibration. The K_d values at 6.3 months may or may not be at equilibrium, a condition assumed for the K_d construct, and as such, these values either represent or underestimate the true steady-state K_d values.

Table 5. K_d data for ^{14}C-carbonate (mL/g) on different solids as a function of time

Solid	1.7h	19.1h	24.6h	4.8d	13.1d	6.3m
SRS clayey subsurface sediments	9.68 ± 2.1	17.9 ± 2.8	27.6 ± 3.9	29.9 ± 4.47	24.3 ± 3.48	> 372 ± -
SRS sandy subsurface sediments	0.86 ± 1.2	1.62 ± 1.3	1.54 ± 1.2	0.56 ± 1.1	1.43 ± 1.2	8.64 ± 1.9
36-year Old Concrete	242 ± 613	220.0 ± 23.0	33.5 ± 14.7	229.0 ± 33.9	197 ± 36.7	> 2850 ± -
Reducing Grout	1.78 ± 2.27	6.77 ± 10.7	3.75 ± 11.4	11.2 ± 12.2	17.1 ± 10.6	39.2 ± 14.7

4.2 DESORPTION EXPERIMENT

In all but one of the six desorption experiments very little ^{14}C-carbonate was desorbed from the solid phase into solution (Figure 6). The one exception was the case of phosphate addition to the 36-year-old concrete. It should be noted that a much greater phosphate concentration was used in this study than is expected in the SRS subsurface. High anion concentrations were selected to provide insight into how strongly the ^{14}C-carbonate was retained by these various solid phases. The desorption experiment demonstrated that the ^{14}C-carbonate was sorbed strongly to the sediment and cementitious materials surfaces, even in the presence of extraordinarily high competing anion concentrations (except phosphate). The competition between phosphate and carbonate has been studied previously on mineral surfaces (Rahnemaie et. al., 2007). Rahnemaie et. al., (2007) reported finding that phosphate outcompetes carbonate especially at higher pH values. The pH of the cement-water mixture was between 8 and 9, whereas the clay-water mixture was between pH 5 and 6. Thus, phosphate is likely outcompeting the carbonate only in the case of the cement where the pH is higher and the phosphate is known to sorb more strongly. Although the rates of desorption were not measured, it can be qualitatively seen from this work that desorption is appreciably slower than adsorption (Figure 2 through Figure 5).

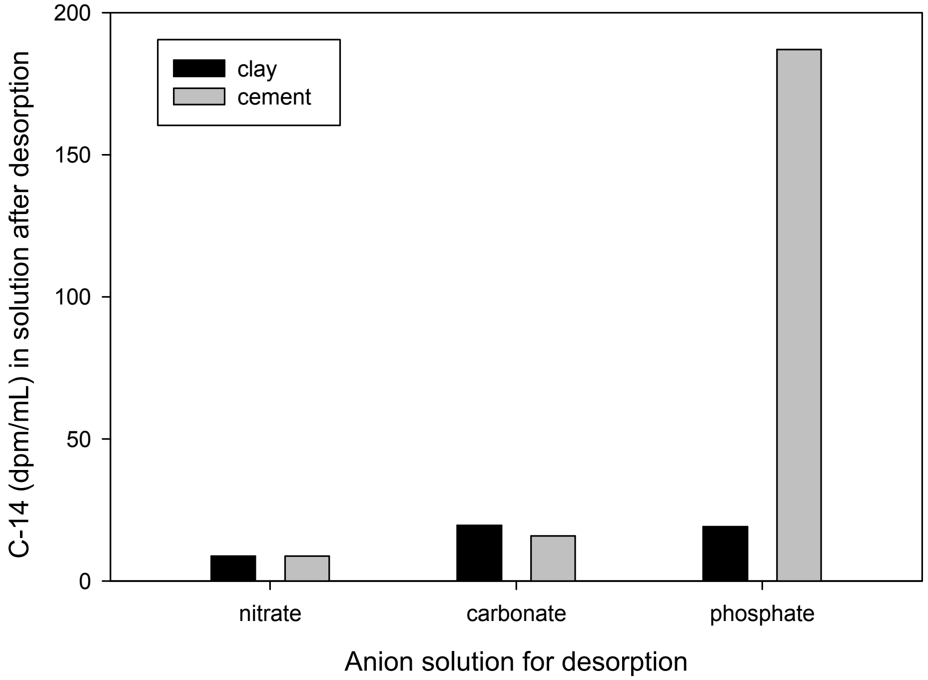

Figure 6. Activity of ^{14}C-carbonate in solution after desorption experiment in 0.01M anion (nitrate, carbonate or phosphate) solutions to assess competitive replacement.

For the desorption experiments, the amount of competing anion sorbed by the clayey sediment and 36-year-old concrete is presented in Figure 7. In the presence of the clayey sediment approximately 10% of the nitrate and carbonate were sorbed. In the presence of 36-year-old concrete, 10% of carbonate and 5% of nitrate was sorbed. Unexpectedly, the addition of phosphate resulted in the release of some phosphate from the solids, consequently a negative sorption of phosphate, *i.e.,* desorption of phosphate, was measured.

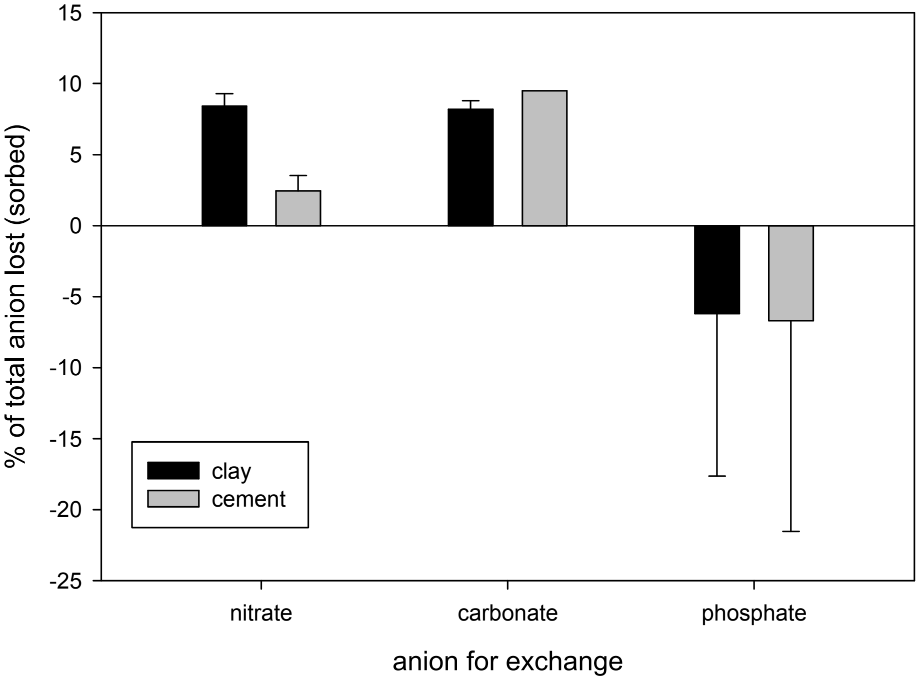

Figure 7. Percent of anion sorbed by the clayey sediment and the 36-year-old concrete during the desorption experiment. About 0.01M anion solution was added of each anion. The negative phosphate values indicate that some phosphate was desorbed from the solid phases upon adding phosphate to the suspensions.

5.0 CONCLUSIONS

Sorption of ^{14}C-carbonate on four solid phases relevant to SRS performance assessments increased over a 189.2 day (6.3 month) period. ^{14}C-carbonate approached 95% sorption on clayey sediment and 36-year-old concrete samples during this 6.3 month period and appeared to have a lower sorption affinity for the sandy sediment (40%), and even lower sorption affinity for the reducing grout (25%). On all four substrates, the K_d values at 6.3 months were clearly much greater than 0 mL/g, ranging from 8.6 mL/g for the sandy sediment to >2800 for the aged concrete. Though it is not clear from the data that sorption equilibrium was achieved, estimates for the apparent K_d values after 6.3 months are as follows: 3000 mL/g for clayey sediments, 10 mL/g for sandy sediments, 30,000 mL/g for concrete and 40 mL/g for reducing grout. It was also demonstrated that sorption and desorption rates were different and that the ^{14}C-carbonate was strongly sorbed onto both clayey sediment and the 36-year-old concrete, indicating that a kinetic sorption model, as oppose to the steady-state K_d model, may be a more accurate description of the ^{14}C-carbonate sorption process.

There are a number of assumptions that transport modelers are required to make in order to incorporate the convenient K_d construct, including that the rate of adsorption is equal to the rate of desorption, sorption does not change as a function of radionuclide concentration, and the system is at steady state (equilibrium; i.e., that a radionuclide is in contact with soil sufficiently long to permit steady state chemical conditions to exist). Data from this study suggest that the last assumption is not appropriate for ^{14}C-carbonate geochemistry. Instead, as groundwater moves through the subsurface sediment (i.e., water pore velocities in the range of 0.5 to 1.0 ft/day are quite typical in SRS sandy sediments), ^{14}C's contact time, in the order of a day, is not sufficiently long to permit steady state to occur. Ideally a kinetic sorption model would be used, but given the limitations of the existing SRS PA models, an "apparent K_d value" after 1 day contact time may be more appropriate than a K_d value at steady state, >6.3 months. This would be an "apparent K_d value" because it is not truly at steady state. Apparent K_d values for sandy sediment would be 1 mL/g, and for clayey sediment, 30 mL/g.

Figure 8 graphically compares these clayey and sandy apparent K_d values versus the recommended values above. Early transient effects for sandy sediments appear to be quite small for sandy sediments; however, for clayey sediments a clear transient effect is present for the first day to 1.5 day time period. Pore velocities in clayey sediments will be much slower than in sandy sediments suggesting that the average value of 30 ml/g may be appropriate. To better define an apparent K_d value for clayey sediments, as mentioned above, a transport analysis employing a local kinetic sorption model should be considered.

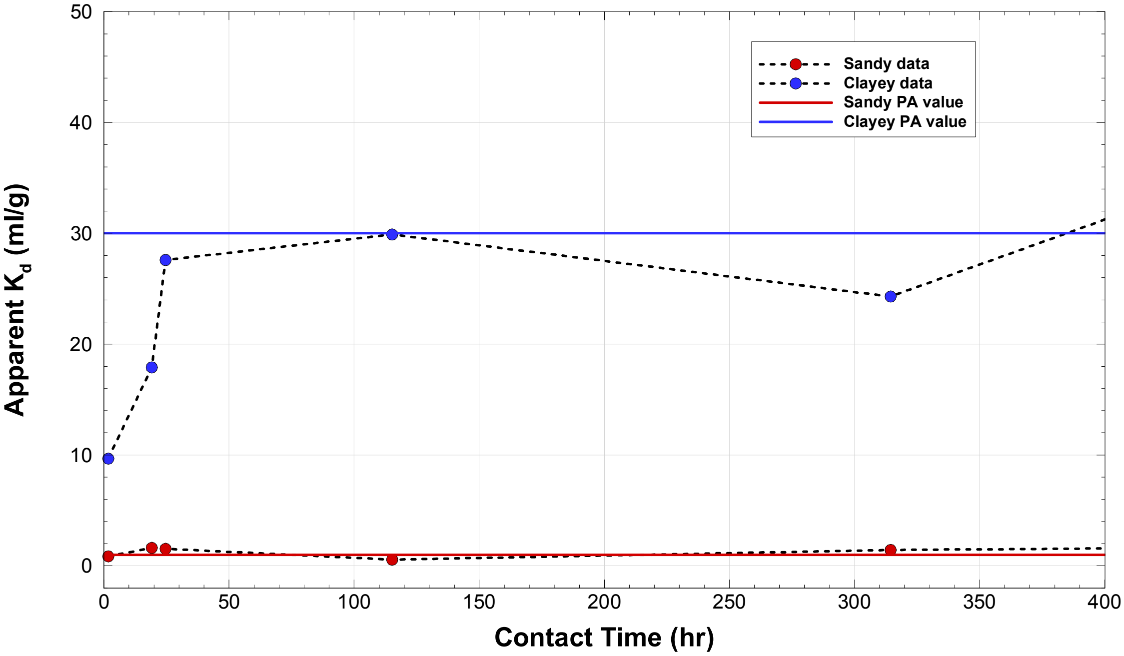

Figure 8. Comparison of Apparent K_d values for SRS Sandy and Clayey sediments versus recommended value for use in PA analyses for C-14.

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APPENDIX A. CARBON-14 RAW DATA AND RESEARCH AND DEVELOPMENT DIRECTIONS

RESEARCH AND DEVELOPMENT DIRECTIONS: MEASURING SORPTION (K_d) OF ^{14}C ON SRS SOILS AND CEMENTITIOUS MATERIALS

PI:
Dan Kaplan/ Kim Roberts
Date:
4/18/08
HAP:
SRNL-EST-2006-00093
Hazards:
Radionuclides
Hazards Mitigation:
Radionuclides: Follow training of Advanced Rad Worker
Objective:

1. Measure $^{14}CO_3^{2-}$ sorption parameters, K_d, on SRS site soils and cementitious materials for applicable to subsurface contaminant transport calculations. There is very little information in the literature on this subject as it relates to acidic soils, as exists at the SRS.
2. Determine the sorption kinetics of $^{14}CO_3^{2-}$ onto these surfaces to assure us that sorption is not kinetically hindered, compromising the application of the K_d construct in reactive transport models. Literature indicates that there may be a significant kinetic component to CO_3^{2-} sorption to sediments.
3. Determine how strongly the sorbed $^{14}CO_3^{2-}$ is retained by these geo-sorbents. This will be accomplished by adding varying anions to systems where $^{14}CO_3^{2-}$ is sorbed. The competitive anions will have varying valences and ionic radii: NO_3^- (ionic radius = 165 x 10^{-12} m), CO_3^{2-} (ionic radius = 164 x 10^{-12} m), and PO_3^{3-} (ionic radius = 29 x 10^{-12} m).

Materials:

1. SRS sandy subsurface sediment
2. SRS clayey subsurface sediment
3. Aged cementitious material (36-year old recovered from SRS structure)
4. Slag cementitious material
5. $^{14}CO_3^{2-}$ spike solution (as sodium carbonate in 0.001 M NaOH) (0.2 µCi/mL or 440,000 dpm/mL
6. uncontaminated SRS groundwater (Par Pond Groundwater)
7. 15ml centrifuge tubes
8. 10-mLdisposable syringes
9. 0.1µm or 0.45µm syringe filters
10. 25mm 0.45µm filters and disposable housings for subset (t=24h) only
11. sample bottles; filter holders
12. 100 mM $NaNO_3$: Using a 100 mL volumetric flask, dissolve 0.85 g of $NaNO_3$ into ~80 mL of MilliQ water, then bring up to volume.
13. 100 mM Na_2CO_3: Using a 100 mL volumetric flask, dissolve 1.06 g of Na_2CO_3 into ~80 mL of MilliQ water, then bring up to volume.
14. 100 mM NaH_2PO_4-H_2O: Using a 100 mL volumetric flask, dissolve 1.38 g of NaH_2PO_4-H_2O into ~80 mL of MilliQ water, then bring up to volume.

Methods:

Sorption Tests (Objectives 1 & 2)

Equilibrating solids with groundwater. This experiment will have duplicate samples for each solid (sandy soil, clayey soil, cementitious material and slag cementitious material) and 6-repls for t=96hour, as noted on Table 1. Do not label and tare tubes in Table 2 – you will simply relabel these and use the tare weights entered in Table 1.

1. Label tubes and record tare weights (without caps) in Table 1.
2. Add 1 ± 0.01g of soil material (Tubes 301 – 328) or 0.1 ± 0.01g of cementitious material (tubes 329 – 357) into 15ml centrifuge tubes. Weight and enter "Solid Wt." into Table 1.
3. Add 10ml ground water to each tube.
4. Place samples on shaker overnight.
5. The next day let solids settle, decant and be careful not to lose solids, error on side of leaving liquids in tube.

Batch adsorption as a function of time

6. Add 0.70mL of $^{14}CO_3^{2-}$ spike solution to 840 mL of Par Pond Groundwater.
7. Move pre-equilibrated solids to rad hood. Add 12 mL of $^{14}CO_3^{2-}$ amended groundwater created in step 6. Also add 12 mL of this amended groundwater to the No-solids Controls (Tube ID #358 359, & 360). Weigh "Tube+Solid+Liq Wt" and record in Table 1. Record date/time in Table 1. Shake by hand all samples vigorously for 5 seconds.
8. Measure pH with litmus paper and record in Table 1 (soils will be pH ~4-5, cements will be pH ~9-12).
9. Shake 3x a day by hand for appropriate duration as indicated in Table 1.

Sorption sample separation

10. Let solids settle (or centrifuge at 4000 rpm for 10 min), decant and be careful not to lose solids, error on side of leaving liquids in tube.
11. Carefully siphon supernatant from 15ml tube and pass through a 0.1µm syringe filter; collecting filtrate in sample bottle to be submitted to Analytical Development section for liquid scintillation counting of ^{14}C. Record "Stop date/time" in Table 1.
12. Save solids (in rad hood) for use in the desorption experiment described below.

Solids Measurements for QA: Mass balance of K_d[1] and Total Recovery of Rads on Solids

13. For samples 305, 306, 333, & 334, separate solids from liquid by passing slurry through 25mm 0.4um filter. Place filter disc and all the solids in labeled and tared (record in Table 1) liquid scintillation vial (20mL). Be sure to include the soil weight that was transferred into the samples. Sample numbers are 405,406,433 & 434, corresponding to the liquid samples of 305, 306, 333, & 334, respectively. By combining the results of these analyses, we will directly measure K_d, as oppose to measuring sorbed by difference in the aqueous phase.

---

[1] We are testing the assumption that the amount of rad can be determined by measuring the amount remaining in the aqueous phase before and after the study. In these steps of the experiment we are preparing solids for direct measurement by liquid scintillation counting: $Kd = A_{solid}/A_{aq}$.

14. Add 1 g of clayey sediment to a tube labeled #401 and 0.1 g of cement to a tube labeled #402. Add 10mL groundwater. Shake vigorously. Pass through a 0.45µm filter. Place filters and solids into tared sample tubes (tubes you will submit to ADS) label #401 and #402. Add 10µL of ^{14}C spike solution to solid on filter.
15. Submit these six solid samples to Analytical Development section for liquid scintillation counting of ^{14}C. It may require that we submit these under separate Travel Copies because these are solid samples, compared to the rest of the samples being aqueous samples.

Desorption Experiments

16. Move tubes 309 – 314 and 337 – 342 into the same rack. Re-label them as shown in Table 2.
17. Add 8 mL of appropriate $NaNO_3$, Na_2CO_3, or Na_3HPO_3 solution, as designated in Table 2. Shake sample vigorously my hand for 5 seconds. Weigh and record weight in Table 2.
18. Measure pH with litmus paper and record in Table 2.
19. Shake by hand 3X a day, at the beginning and end of the work day for one week.
20. Let solids settle to separate solids from liquids.
21. Carefully siphon supernatant from 15ml tube and pass through a 0.1µm syringe filter; collecting filtrate in sample bottle to be submitted to Analytical Development section for liquid scintillation counting of ^{14}C and for ion chromatography analysis for nitrate, carbonate, and phosphate analysis.

Table A-1. Sample descriptions, experimental conditions and raw data for ^{14}C sorption and desorption experiments

ID	SOLID	TIME	REP	TARE WT (G)	SOLID WT (G)	TARE+SOLID+LIQ WT (G)	START DATE/ TIME	STOP DATE/TIME	TIME	^{14}C AT END OF EXPT (DPM/ML)
	Step #			**1**	**2**	**6**	**7**	**11**		
301	Clay	t=0.5h	1	5.43378	1.00053	19.044	4/23/2008 14:17	4/23/08 16:00	1.72	1.72E+02
302			2	5.46006	1.0017	19.046	4/23/2008 14:17	4/23/08 16:00	1.72	1.24E+02
303		t=8h	1	5.43111	1.00298	18.985	4/23/2008 14:17	4/24/08 9:25	19.13	1.13E+02
304			2	5.42024	1.00329	18.986	4/23/2008 14:17	4/24/08 9:25	19.13	9.79E+01
305		t=24h	1	5.40971	1.00134	19.506	4/23/2008 14:17	4/24/08 14:55	24.63	8.25E+01
306			2	5.45244	1.00554	19.041	4/23/2008 14:17	4/24/08 14:55	24.63	7.90E+01
307		t=48h	1	5.41195	1.0018	19.074	4/23/2008 14:17	4/28/08 9:25	115.13	7.39E+01
308			2	5.43011	1.00528	19.001	4/23/2008 14:17	4/28/08 9:25	115.13	7.73E+01
309		t=96h	1	5.45033	1.00118	19.113	4/24/2008 10:05	5/7/08 12:00	313.92	7.74E+01
310			2	5.46006	0.99985	18.985	4/24/2008 10:05	5/7/08 12:00	313.92	9.11E+01
311			3	5.4257	0.99939	18.97	4/24/2008 10:05	5/7/08 12:00	313.92	1.03E+02
312			4	5.43819	1.00558	19.111	4/24/2008 10:05	5/7/08 12:00	313.92	9.22E+01
313			5	5.43576	1.0028	18.728	4/24/2008 10:05	5/7/08 12:00	313.92	8.59E+01
314			6	5.42366	1.00095	18.986	4/24/2008 10:05	5/7/08 12:00	313.92	7.71E+01
315		t=1mo	1	5.44616	1.00868	19.277	4/24/2008 10:05	10/30/08 15:00	4540.92	<8.40E+00
316			2			19.074	4/24/2008 10:05	10/30/08 15:00	4540.92	<8.42E+00
317	Sand	t=0.5h	1	5.63509	0.99731	19.066	4/23/2008 14:17	4/23/08 16:00	1.72	2.36E+02
318			2	5.43704	1.00332	18.929	4/23/2008 14:17	4/23/08 16:00	1.72	2.41E+02
319		t=8h	1	5.62165	1.00687	19.203	4/23/2008 14:17	4/24/08 9:25	19.13	2.20E+02
320			2	5.49139	0.99907	19.06	4/23/2008 14:17	4/24/08 9:25	19.13	2.32E+02
321		t=24h	1	5.59132	1.00852	19.246	4/23/2008 14:17	4/24/08 14:55	24.63	2.29E+02
322			2	5.45095	1.00499	18.951	4/23/2008 14:17	4/24/08 14:55	24.63	2.25E+02
323		t=48h	1	5.59617	1.00747	19.103	4/23/2008 14:17	4/28/08 9:25	115.13	2.43E+02
324			2	5.47317	1.00587	18.971	4/23/2008 14:17	4/28/08 9:25	115.13	2.45E+02
325		t=96h	1	5.59937	1.00088	19.229	4/24/2008 10:05	5/7/08 12:00	313.92	2.27E+02
326			2	5.61906	1.00307	19.146	4/24/2008 10:05	5/7/08 12:00	313.92	2.31E+02
327		t=1mo	1	5.60912	1.00847	19.251	4/24/2008 10:05	10/30/08 15:00	4540.92	1.48E+02
328			2	5.44521	1.00099	19	4/24/2008 10:05	10/30/08 15:00	4540.92	1.54E+02

ID	SOLID	TIME	REP	TARE WT (G)	SOLID WT (G)	TARE+SOLID+LIQ WT (G)	START DATE/ TIME	STOP DATE/TIME	TIME	^{14}C AT END OF EXPT (DPM/ML)
329	Cement	t=0.5h	1	5.56766	0.09975	18.236	4/23/2008 14:17	4/23/08 16:00	1.72	2.49E+02
330			2	5.56729	0.100008	17.83	4/23/2008 14:17	4/23/08 16:00	1.72	5.15E+01
331		t=8h	1	5.43688	0.09914	17.703	4/23/2008 14:17	4/24/08 9:25	19.13	9.12E+01
332			2	5.45196	0.10345	17.713	4/23/2008 14:17	4/24/08 9:25	19.13	2.27E+03
333		t=24h	1	5.43749	0.10276	17.655	4/23/2008 14:17	4/24/08 14:55	24.63	2.13E+02
334			2	5.43723	0.10306	17.701	4/23/2008 14:17	4/24/08 14:55	24.63	1.86E+02
335		t=48h	1	5.45014	0.1007	17.963	4/23/2008 14:17	4/28/08 9:25	115.13	8.18E+01
336			2	5.62069	0.10308	17.831	4/23/2008 14:17	4/28/08 9:25	115.13	9.55E+01
337		t=96h	1	5.41304	0.101161	17.678	4/24/2008 10:05	5/7/08 12:00	313.92	1.22E+02
338			2	5.43532	0.10374	17.829	4/24/2008 10:05	5/7/08 12:00	313.92	1.18E+02
339			3	5.59102	0.10106	17.605	4/24/2008 10:05	5/7/08 12:00	313.92	1.66E+02
340			4	5.55216	0.100149	17.832	4/24/2008 10:05	5/7/08 12:00	313.92	1.31E+02
341			5	5.4176	0.101661	18.728	4/24/2008 10:05	5/7/08 12:00	313.92	4.13E+01
342			6	5.43664	0.10517	17.716	4/24/2008 10:05	5/7/08 12:00	313.92	1.68E+02
343		t=1mo	1	5.43582	0.1008	17.701	4/24/2008 10:05	10/30/08 15:00	4540.92	<1.03E+01
344			2	5.58685	0.10138	17.769	4/24/2008 10:05	10/30/08 15:00	4540.92	<1.03E+01
345	Slag-cement	t=0.5h	1	5.61444	0.10082	18.013	4/23/2008 14:17	4/23/08 16:00	1.72	2.70E+02
346			2	5.61371	0.10029	17.888	4/23/2008 14:17	4/23/08 16:00	1.72	2.35E+02
347		t=8h	1	5.57255	0.10106	17.873	4/23/2008 14:17	4/24/08 9:25	19.13	2.41E+02
348			2	5.44971	0.10022	17.719	4/23/2008 14:17	4/24/08 9:25	19.13	2.42E+02
349		t=24h	1	5.58325	0.1012	17.878	4/23/2008 14:17	4/24/08 14:55	24.63	2.46E+02
350			2	5.42593	0.10206	18.632	4/23/2008 14:17	4/24/08 14:55	24.63	2.49E+02
351		t=48h	1	5.43036	0.10189	17.647	4/23/2008 14:17	4/28/08 9:25	115.13	2.39E+02
352			2	5.41921	0.10336	17.691	4/23/2008 14:17	4/28/08 9:25	115.13	2.27E+02
353		t=96h	1	5.44168	0.1013	17.658	4/24/2008 10:05	5/7/08 12:00	313.92	2.29E+02
354			2	5.62307	0.10514	17.839	4/24/2008 10:05	5/7/08 12:00	313.92	2.15E+02
355			3	5.59433	0.1	17.801	4/24/2008 10:05	5/7/08 12:00	313.92	2.25E+02
356		t=1mo	1	5.43045	0.10236	17.696	4/24/2008 10:05	10/30/08 15:00	4540.92	1.90E+02
357			2	5.53511	0.10114	17.754	4/24/2008 10:05	10/30/08 15:00	4540.92	1.94E+02
358	No-Solids Control	t=96h	1	5.412	0	17.451	4/24/2008 10:05	5/7/08 12:00	313.92	2.61E+02
359			2	5.611	0	17.643	4/24/2008 10:05	5/7/08 12:00	313.92	2.58E+02
360			3	5.449	0	17.484	4/24/2008 10:05	5/7/08 12:00	313.92	2.46E+02

Table A-2. Desorption Experiment

ID	ID IN TABLE 1	SOLID	EXCHANGE ANION	REP	NO_3 (PPM)	CO_3 (PPM)	PO_4 (PPM)	^{14}C (DPM/ML)
Instruction step:			2		2	3		
501-N	309	Clay	Nitrate	1	6020			8.84E+00
502-N	310			2	5940			8.84E+00
503-C	311		Carbonate	1		1070		1.91E+01
504-C	312			2		1060		2.01E+01
505-P	313		Phosphate	1			10300	2.01E+01
506-P	314			2			12000	1.80E+01
507-N	337	Cement	Nitrate	1	6420			8.85E+00
508-N	338			2	6320			8.86E+00
509-C	339		Carbonate	1		1050		1.59E+01
510-C	340			2		1050		No Data
511-P	341		Phosphate	1			10100	2.79E+02
512-P	342			2			12300	9.41E+01
513-N	none		nitrate	total	6530			No Data
514-C	none		Carbonate	total		1160		No Data
515-P	none		Phosphate	total			10500	No Data

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