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RETENTION:
Permanent

PARTITIONING OF DISSOLVED RADIONUCLIDES TO CONCRETE UNDER SCENARIOS APPROPRIATE FOR TANK CLOSURE PERFORMANCE ASSESSMENTS

Daniel I. Kaplan
John M. Coates

DECEMBER 21, 2007

Savannah River National Laboratory
Washington Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under
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12/21/2007

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LIST OF ACRONYMS

$CaCO_3$	Calcite
$Ca(OH)_2$	Portlandite
DDI water	Distilled deionized water
PA	Performance Assessment
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

1.0 EXECUTIVE SUMMARY

The Savannah River Site (SRS) is conducting a performance assessment (PA) to evaluate the long-term impacts of closing waste tanks by filling them with reducing grout. The objective of this task was to quantify the extent that radionuclides sorb to cementitious materials. There were four separate studies conducted for this task: Batch Sorption Study, Approach to Equilibrium Study, Desorption Study, and Influence of Reducing Grout on Aqueous Chemistry Study. The first was to measure K_d values (ratio of radionuclide solid's concentration divided by the radionuclide liquid's concentration) for use in the PA. This study measured K_d values for 15 radionuclides, three solids (Aged Cement, Reducing Grout, and Aged Reducing Grout), and two aqueous phases (portlandite-saturated solution to simulate leachate from a young cement, and a calcite-saturated solution to simulate leachate from an older cement). With few exceptions, the measured reducing grout and aged cement K_d values were greater than the values presently used in SRS PAs. A look-up table with generally much greater reducing grout K_d values and moderately greater oxidized cement K_d values is included in the appendix. Kinetic studies revealed that the cementitious materials (ad)sorb radionuclides in the order of days, and desorbed radionuclides in the order of hundreds to thousands of years. These are ideal attributes for mitigating the migration of radionuclides. Furthermore, it indicates that past PAs were very conservative by describing radionuclide-cement interactions with a K_d or apparent solubility term. Should future PAs need to be more accurate or less conservative, the inclusion of the desorption kinetic terms would be appropriate.

2.0 INTRODUCTION

DOE sites are presently evaluating the use of various cementitious materials for closing tanks. The extent that they immobilize radionuclides has been shown to be strongly dependent on the ingredients and recipes used in the cementitious materials (Bradbury and Sarott 1995; Krupka and Serne 1998). Therefore it is difficult to take cement K_d values from the literature and apply to another environment. When this is the only alternative, it introduces a great deal of uncertainty. Such uncertainty often results in greater cost associated with the engineered barriers used to meet performance objectives.

The objectives of this project were to make radionuclide K_d measurements with site-specific cementitious materials. These materials included an SRS reducing grout and a 40 year old concrete recovered from an SRS building. Additionally, the rate of sorption and desorption were measured for several radionuclides. More specific objectives are provided in the Materials and Methods section (Section 3.0). It is important to note that this study does not address release of the radionuclides from the contaminated zone within a closed tank. Instead it deals with the geochemical parameters of the radionuclides once they are released into the aqueous phase. Radionuclide release from the sludge in the contamination zone is described by Denham (2007).

3.0 MATERIALS AND METHODS

3.1 MATERIALS

The same basic materials were used for these studies: Batch Sorption Study, Approach to Equilibrium Study, Desorption Study, and Influence of Reducing Grout on Aqueous Chemistry.

- Solids: Aged Concrete from which the Aged Cement was collected, Reducing Grout, and Aged Reducing Grout
- Aqueous Phases: Calcite ($CaCO_3$) Saturated Solution (Oxygenated and Deoxygenated), Portlandite ($Ca(OH)_2$) Saturated Solution (Oxygenated and Deoxygenated)
- Radionuclides: gamma standard suite [^{241}Am(III), ^{109}Cd(II), ^{139}Ce(III), ^{60}Co(II), ^{137}Cs(I), ^{230}Hg(II), ^{113}Sn(IV), ^{89}Sr(II), and ^{88}Y(III)], ^{129}I, ^{238}Pu(IV/V), ^{239}Np(V), ^{231}Pa, ^{99}Tc(VII), and ^{235}U

The isotopes used in these measurements were selected for ease of measurement and their availability, and as such often differed from those of interest to the performance assessment. Isotopes of a given element sorb to sediments in a similar manner.

3.1.1 Cementitious Materials

Reducing Grout was prepared by Chris Langton (SRNL) and was identified as sample OPDEXE-X-P-O-BS. It contained:

210 lb/yd^3 slag,
60 gallons/yd^3 (500 lbs/yd^3) of water,
75 lb/yd^3 of Portland cement,
375 lb/yd^3 fly ash,
2300 lb/yd^3 sand,
90 oz/yd^3 of Adva-380,
275 g/yd^3 of KelcoCrete, and
2.1 lb/yd^3 sodium-thiosulfate.

This material was initially broken up with a chisel and hammer to ~1-cm sized particles. Then ~100 g of the 1-cm sized particles were placed in a jaw crusher (Retsch Jaw Crusher Type BB51 with tungsten carbide plates) for ten minutes. The jaw crusher samples were then placed in a shatter box (Spec 8510 Shatterbox) for 10 seconds. The <1000-µm and >75-µm sieve fraction was used for these studies. The Brunauer, Emmett, Teller (BET) surface area, pH and Eh of the Reducing Grout are reported in Table 1.

Aged Reducing Grout was made by oxidizing Reducing Grout with ozone purged distilled and deionized water (DDI water) (30 mg/L dissolved oxygen). Approximately 10 g of the

Reducing Grout was added to a 150 ml Corex® centrifuge tube followed by the addition of 150 ml of the oxidizing solution. The suspension was mixed on a platform shaker for one to two days. This procedure was repeated for an additional two treatments. The oxidation-reduction potential of the solution after treatment remained constant at 110 mV. The oxidized-reducing grout was separated from the oxidizing solution and placed in a hood to air dry. This method of "aging" the grout did not permit such important aging processes as microbial degradation, cracking, and sulfate attack to occur in a manner expected in field-aged materials. But as will be discussed in Section 4.4, some important water chemistry parameters (e.g., Eh and dissolved Fe and S) did change in a manner commensurate with the aging of Reducing Grout, i.e., it reduces the environment less.

Aged Cement was collected from a 40 year old concrete core taken from a building pad located on the SRS. To separate the aggregate from the cement, a portion of the 3-inch diameter core was crushed with a hammer and then the cement was loosened from the aggregate with the use of an awl and screw driver. Separation of these two phases within the concrete was relatively easy to accomplish; the task took about one hour per core. After separation, the cement phase was broken up into smaller more uniform particles with a Spex 8510 Shatterbox. The <1000 µm and >75 µm sieve fraction was used for these experiments. It is important to note that the cement and not the aggregate was used in these measurements.

Table 1. 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
Aged Reducing Grout	7.11 ± 0.02	11.24	110 to 325
Aged Cement	5.88 ± 0.02	11.99	347

[a] The Clemson University batch of Aged Reducing Grout had an Eh reading of 325 mV, the SRNL batch had a Eh reading of 110 mV. These values should be identical but may be attributed to how the two measurements were made (SRNL let the mixture sit for 1 hr prior to measurement, Clemson University did not).

3.1.2 Aqueous Phases

Portlandite ($Ca(OH)_2$) Saturated Leaching Solution (oxygenated and deoxygenated): This solution was used in the sorption tests to simulate the first and second stage of cement aging.[1] During these cement aging stages, $Ca(OH)_2$, and calcium-silicate-hydrate gels are the key solid phases controlling aqueous leachate chemistry.

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[1] Cement is described in the performance assessment as aging in three progressive stages. These stages have unique mineralogy and leachate chemical conditions. How cement aging is treated in the performance assessment is described in Kaplan (2006).

Because CO_2 in air is very soluble in water at high pH and the resulting dissolved carbonate (CO_3^{2+}) will precipitate as calcite in the $Ca(OH)_2$- saturated solution, care was taken to minimize contact of the solution with atmospheric air. Excess solid $Ca(OH)_2$ was undesirable because it would buffer the pH at an abnormally high pH level.

Distilled deionized (DDI) water was used for the preparation of both oxygenated and deoxygenated $Ca(OH)_2$-saturated solutions. The DDI water was boiled for approximately 30 minutes and purged with high purity N_2 at approximately 25 ml/sec to remove dissolved CO_2 and O_2. Approximately 1.35 g of reagent grade $Ca(OH)_2$ was added per liter of solution, followed by an ozone purge for approximately two minutes to restore dissolved O_2 to the oxygenated solution. The deoxygenated solution was stored under N_2 in a glove bag. Additionally, it was necessary to periodically skim off precipitates that formed at the water/air interface.

Calcite-Saturated Leaching Solution (oxygenated and deoxygenated): This solution was used in the sorption tests to simulate the third stage of cement aging. During this stage, portlandite has been fully dissolved/reacted and the solubility or reactions of the calcium-silicate-hydrate gel with the infiltrating water controls the pH of the cement pore-water/leachate. The pH continues to decrease until it reaches the pH of the background sediment, pH 5.5 at the SRS. Radionuclides tend to sorb least during this stage.

By preparing the solution at a slightly elevated temperature the possibility of calcite precipitation during the test at room temperature will be minimized. (Calcite undergoes retrograde solubility.) There was no need to minimize contact of this solution with the atmosphere. Calculated equilibrium values for this solution are: pH = 8.3, Ca^{2+} = 20 mg/L, total inorganic carbon = 58 mg/L, PCO_2 = 0.0003 atm (fixed).

Calcite-saturated solutions were prepared by adding excess powdered reagent grade calcite to distilled-deionized (DDI) water and stirring for approximately 24 hr at a slightly elevated room temperature, approximately 25-30 ^{o}C. Solutions were filtered at 0.45 µm using 90 cm nylon filters clamped within a filtering apparatus. Solution pH was ~8.4. Deoxygenated calcite-saturated solutions were prepared as noted above after first purging the DDI water with high purity N_2 (Clemson University) or Ar (SRNL) gas at a flow rate of 25 ml/sec for approximately 30 min for each 3-liter preparation. These solutions were filtered using the above apparatus under a N_2 blanket. Following preparation, the deoxygenated calcite-saturated solutions were stored in a glove bag under N_2.

3.1.3 Radionuclides

Radionuclides used in this study were gamma standard suite (^{241}Am(III), ^{109}Cd(II), ^{139}Ce(III), ^{60}Co(II), ^{137}Cs(I), ^{230}Hg(II), ^{113}Sn(IV), ^{89}Sr(II), and ^{88}Y(III)), ^{129}I, ^{238}Pu(IV/V), ^{239}Np(V), ^{231}Pa, ^{99}Tc(VII), and ^{235}U. They were purchased from Eckert & Ziegler Analytics (Atlanta Georgia), except ^{238}Pu, which originated from site activities and was provided by David Hobbs (SRNL).

I, Tc, Np, Pu, and U were included in these tests because they were found to be important risk drivers in preliminary calculations. Am, Cd, Ce, Co, Cs, Hg, Pa, Sr, Sn, and Y were included because a great deal of additional information could be collected from these tests with relatively little additional effort, i.e., they could be measured together using a single cocktail of gamma-emitting isotopes. These gamma emitters were analyzed to provide information about the sorption of some radionuclides of interest to the performance assessment (Co, Ce, Cs, Am, Pa, Sr, and Y), as well as provide indirect information for surrogate radionuclides. For example, they provided insight into how monovalent cations (Cs), divalent cations (Hg, Co, and Sr), trivalent cations (Ce and Am), and tetravalent cations (Sn) sorb to cementitious materials.

3.2 BATCH SORPTION STUDY

3.2.1 Objectives – Batch Sorption

The objective of this experiment was to measure radionuclide K_d values (ratio of radionuclide solid's concentration divided by the radionuclide liquid's concentration) for all the radionuclides listed in Section 3.1.3 under conditions appropriate for the tank closure performance assessment. Experimental conditions were created to simulate an oxidizing cementitious environment early in its aging process (Stage 1 & 2) and later in its aging process (Stage 3) (these stages are described in more detail in Kaplan 2006). Similar tests were conducted with Reducing Grout and Aged Reducing Grout. Values from these tests were used to provide site-specific K_d values for use in the performance assessment.

3.2.2 Materials – Batch Sorption

- Cementitious Solid Phases: SRS Aged Cement, Reducing Grout, and an artificially-Aged Reducing Grout,
- Aqueous phase chemistry: portlandite- and calcite-saturated solutions to simulate Stages 1 & 2, and Stage 3 in the cement lifecycle, respectively,

- Radionuclides: Am, Cd, Ce, Co, Cs, Hg, I, Np, Pa, Pu, Sn, Sr, Tc, U, and Y

3.2.3 Methods – Batch Sorption

There were four near identical experiments conducted in which different radionuclides were added to the same three cementitious materials. The radionuclides in these four near identical experiments were:

1. ^{237}Np, ^{231}Pa, ^{125}I and ^{235}U,
2. ^{99}Tc,
3. ^{238}Pu (results not reported in this memorandum),

a suite of gamma-emitting radionuclides, ^{241}Am(III), ^{109}Cd(II), ^{139}Ce(III), ^{60}Co(II), ^{137}Cs(I), ^{230}Hg(II), ^{113}Sn(IV), ^{89}Sr(II), and ^{88}Y(III).

Radionuclides were added in these groupings to ease analysis. Each of these experiments was conducted in an oxidizing environment (on the lab counter top) and a reducing environment (within an N_2 atmosphere at Clemson University or an Ar atmosphere at SRNL).

Batch sorption tests were conducted in a suspension including 0.5 g solid (Reducing Grout, Aged Reducing Grout, and Aged Cement) and 12 mL solution (calcite-saturated or portlandite-saturated). Prior to adding the radiological spike solutions, each solid was pre-equilibrated with the appropriate solutions in an effort to bring the suspension to a chemical steady state. Pre-equilibration was accomplished by adding approximately 30 mL of the appropriate solution to the respective solids and shaking for a minimum of 48 hrs, followed by centrifugation at 2000 rpm for 10 min, decantation of the solution, followed by a second addition of the appropriate solution and shaking for 1 day, followed by centrifugation and decantation. This procedure was replicated for a third 1-hr equilibration period. The resulting suspension was then spiked with ~330 µL of a stock radiological solution. All spiked solutions, except Tc and I, were then pH adjusted by adding ~500 µL of 1 M NaOH. This was necessary because the background solutions for the spikes were acidic. Spiked suspensions were mixed twice daily by vigorously shaking for ~10 seconds. At the end of this spike-equilibration period, the solids were permitted to settle for 1 hr and then the aqueous phase of each tube was passed through a 0.1 µm filter. These solutions were then analyzed for their respective radionuclides using traditional analytical techniques.

All tests were conducted in triplicate. A positive control was included with each set of experiments; "no-solids" control samples that were used to determine if precipitation of the radionuclides occurred during the experiments. K_d values of I, Np, Pa, Pu, Tc, and U were calculated using Eq. 1, which calculates sorption by subtracting the concentration of radionuclide added from the concentration remaining in solution at the end of the one-week equilibration period:

$$K_d = \frac{(C_i - C_f) \times V}{C_f \times m_{solids}} \qquad \text{(Eq. 1)}$$

where C_i and C_f are the aqueous concentrations of the initial and the final equilibrium concentration of each radionuclide (Ci/mL); V = volume of liquid in the final equilibrated suspension (mL); and m_{solids} is the solids mass (g). K_d values of the gamma emitting radionuclides, Am, Cd, Co, Ce, Cs, Hg, Sn, Sr, and Y were measured directly. The K_d value was calculated from direct measurements of the concentrations on the solids and concentrations in the liquids (Eq. 2):

$$K_d = \frac{C_{solids}}{C_f} \qquad \text{(Eq. 2)}$$

where C_{solids} is the radionuclide concentration measured on the solids (Ci/g) and C_f is the radionuclide concentration in the aqueous phase at the end of the sorption experiment

(Ci/mL). Supporting data, including blank controls, standards, and calibration data, are presented in Appendix B.

3.3 APPROACH TO EQUILIBRIUM STUDY

3.3.1 Objectives – Approach to Equilibrium

The objective of this study was to determine the rate at which radionuclides sorb to cementitious materials. The reason these measurements were made was to determine if the assumption of steady state partitioning between the radionuclides and cementitious materials was reasonable. The measurements were also made to permit comparison with the desorption rates described below in Section 3.4. When using K_d it is assumed that adsorption and desorption rates are equal.

3.3.2 Materials – Approach to Equilibrium

The solid phases used in this study were the Aged Cement and the Reducing Grout. The aqueous phase in this study was calcite-saturated solution. The radionuclides used in this study were the gamma suite (^{241}Am(III), ^{109}Cd(II), ^{139}Ce(III), ^{60}Co(II), ^{137}Cs(I), ^{230}Hg(II), ^{113}Sn(IV), ^{89}Sr(II), and ^{88}Y(III)). All of these materials are described in more detail in Sections 3.1.1, 3.1.2, and 3.1.3.

3.3.3 Methods – Approach to Equilibrium

A series of 39 samples were used in this study:

(2 cementitious materials x 6 contact durations x 3 replicates) + (1 no-solids control in calcite saturated solution x 3 replicates) = 39 samples.

45 mL of the appropriate equilibration solution was added to each triplicated Aged Cement and Reducing Grout sample. A 0.5 mL mixed gamma spike was added to each tube. This was quickly followed by a 0.501 mL 4 M NaOH for pH adjustment to the original solution pH, pH range of 8.8 and 9.4. At the appropriate contact time, solids were separated from liquids by centrifuging at 2000 rpm for 15 min. 40 mL of the centrifugate was analyzed by regular gamma spectroscopy for the concentrations of radionuclides. The controls were recovered after 24 hr.

3.4 DESORPTION STUDY

3.4.1 Objectives – Desorption

The objective of this study was to determine if the rate of desorption was the same as the rate of (ad)sorption of radionuclides. This is important because reactive transport studies implicitly assume that the two processes occur at the same rate when they use the K_d construct. Furthermore, if different rates were obtained, then it may be more accurate to describe radionuclide desorption from cementitious materials using a kinetic model, instead of a steady-state model (K_d)[2].

3.4.2 Materials – Desorption

The solids used in this study were Reducing Grout and Aged Cement. The liquid used was a calcite-saturated solution for the Aged Cement and a deoxygenated calcite for the Reducing Grout. The radionuclides used in this study were the gamma suite (^{109}Cd(II), ^{60}Co(II), ^{139}Ce(III), ^{230}Hg(II), ^{113}Sn(IV), ^{137}Cs(I), ^{241}Am(III) and ^{89}Sr(II)). All of these materials are described in more detail in Sections 3.1.1, 3.1.2, and 3.1.3.

3.4.3 Methods – Desorption

Approximately 1 g of solid phase recovered from the Approach to Equilibrium Study (Contact time = ~7 days) was removed from the appropriate centrifuge tubes and wet packed into respective 34 mm x 13 mm OD x 11 mm ID polypropylene chromatography columns. These columns were fitted with 1/8" x 1/16" a Kynar tube fitting (Cole Parmer 30303-14 and a 1/16" barb fitting, Upchurch Scientific P 854X). The column was connected to a peristaltic pump system (Cole Parmer Model 7553-80 fitted with an Easy Load Masterflex® pump head, Model 7518-10 and a Masterflex Speed Controller) with Norprene size-13 tubing. Flow rates for the desorption study were 0.73 to 0.75 ml/min. This flow rate is greater than the expected flow rate at the Tank Farm, but it was selected to provide chemical conditions that would provide a scenario with regard to leaching the greatest mass of radionuclides from the solids. By maintaining low concentrations of aqueous radionuclides, we promoted desorption/dissolution from the solid phase.

The columns were connected to separate gamma detectors in the vertical position and held in place with the use of duct tape. Total gammas detected for each of the sorbed radionuclides were converted to gamma/sec detected for an initial period and for an additional 13 intervals covering a time span of approximately nine days. A calcite-saturated solution was pumped through the column containing the Aged Cement and a deoxygenated calcite solution was pumped through the column containing the Reducing Grout.

Because some of the radionuclide concentrations changed appreciably during the counting duration, it was necessary to correct some of the counts to a single meaningful value. For example, Sr values had to be corrected because the rate of desorption was high and the amount on the column at the start of the counting period was significantly more than the concentration at the end of the counting period. Other radionuclides that did not desorb from the column at fast rates, such as Sn, Ce, and Am, did not require this correction.

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[2] By using a Kd term instead of a slow desorption rate term, the risk will be overestimated (yielding a conservative estimate for the groundwater PA scenario).

3.5 INFLUENCE OF REDUCING GROUT ON AQUEOUS CHEMISTRY

3.5.1 Objectives – Reducing Grout's Aqueous Environment

The objective of this study was to determine the rate that reducing grout changes the chemistry of its aqueous environment. This study was set up to provide some guidance as to the general rate at which a reducing environment is created by reducing grout. This is important because if groundwater takes a fast route through the reducing grout in the tank, such as a crack, it is possible that the contact time would not be sufficient to convert the water from an oxidized to a reduced state. Water in the oxidized state would permit some radionuclides (e.g., Np, Pu, Tc, and U) to travel quicker than if it remained in the reduced state.

3.5.2 Materials – Reducing Grout's Aqueous Environment

Three solids were used in this study: Aged Cement, Reducing Grout, and Aged Reducing Grout (described in more detail in Section 3.1.1). DDI water was used as the aqueous phase.

3.5.3 Methods – Reducing Grout's Aqueous Environment

Approximately 10 g of Aged Cement, Reducing Grout, and Aged Reducing Grout were placed in 50-mL glass jars containing 25 mL of DDI water and a stir bar. The containers were placed on stir plates. Air was sparged into the Aged Cement and Aged Reducing Grout containers. The Reducing Grout suspension was sealed shut and periodically hand mixed. One measurement was made after 14 days of equilibrating of the solution cation (by inductively couple plasma – emission spectroscopy), anions (by ion chromatography), total inorganic carbon (by infrared carbon analysis), and pH, Eh, and conductivity (by probe analysis). A second test was set up using only Reducing Grout and pH, Eh and electrical conductivity was measured nine times over the course of three days. A positive pressure of N_2(*gas*) was pumped into the gas space above the Reducing Grout suspension.[3]

4.0 RESULTS

4.1 BATCH SORPTION STUDY

Before discussing the results, it is important to mention that the K_d values, as they are defined in Equations 1 and 2, include not only adsorption or absorption, but also (co)precipitation. Some (co)precipitation of the radionuclides was noted in the control samples that did not include any solids. That is to say, aqueous radionuclide concentration decreases were observed in the absence of solids. Therefore the measured K_d values, did not describe only readily reversible sorption reactions, as is implicitly implied by this construct. Instead, this process and some (co)precipitation were measured; (co)precipitation tends to have a much

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[3] Changed the experimental method of maintaining a reducing environment because the first method, sealing the container from air, did not permit the Eh to drop very low. The second method of pumping N_2(*gas*) into the gas space above the suspension yielded a lower and more representative Eh.

faster forward reaction (precipitation), than a backward reaction (dissolution). The implications of this are that the resulting K_d values when used in reactive transport modeling will underestimate the true retardation of the contaminant. Furthermore, this would provide a conservative value with respect to the groundwater pathway.

Measured K_d results are presented in Table 2. There are some general trends in this data.

- K_d values generally increased in the following order of valence state:

  $$\begin{gathered} \text{-I } (I^-, TcO_4^-) < \text{+I } (Cs^+) < \text{+II } (Cd^{2+}, Co^{2+}, Hg^{2+}, Sr^{2+}, \text{ and } UO_4^{2+}) \\ < \text{+III } (Am^{3+}, Ce^{3+} \text{ and } Y^{3+}) = \text{+IV } (Sn^{+4}\ Pu^{4+}) \end{gathered} \qquad \text{(Eq. 3)}$$

  This trend is largely consistent with first principles of geochemistry.
- K_d values measured in the Stage 1 & 2 simulant, portlandite-saturated solution, were almost always higher than those measured in the Stage 3 simulant, calcite-saturated solution. This is consistent with expected results and the conceptual model put forth by Bradbury and Sarott (1995). It should be kept in mind that the conceptualized "older" cement consists primarily of calcium-silicate-hydrate gels, which is unlike that used in this study. For this reason, it is likely that the "aged" system may have sorbed more than they would in nature. As a consequence, the values for the calcite-saturated system will over-estimate sorption in the true "aged cement."
- K_d values in the Reducing Grout were generally much larger than those in the Aged Cement, even for some radionuclides that do not have multiple valence states. Some notable higher Reducing Grout K_d values, as compared to Aged Cement, are Am, Cd, Ce, Co, Hg, Np, Pa, Sn, Tc, U, and Y. The exceptionally high Reducing Grout K_d values for the soft metals (Cd, Hg, Sn), and all three trivalent elements (Am, Ce, and Y), are likely due to the formation of strong complexes with sulfide in the Reducing Grout.
- For the radionuclides which have varying oxidation states (Np, Pa, Pu, Tc, and U), K_d values were greater with the Reducing Grout than the Aged Cement. One exception was for Pu, in which the Reducing Grout unexpectedly had a much lower K_d value. It also appears that some oxygen had creped into the reducing environment of the Tc experiment because the amount of Tc sorbed to the Reducing Grout was less than expected, based on it being in equilibrium with the sparingly soluble Tc_3S_{10} phase (Lukens et al. 2002).
- For the portlandite-saturated solution, Aged Reducing Grout K_d values were almost always less than those of the Reducing Grout, except for Pu. This is not surprising because not only was the Reducing Grout oxidized with ozone, but during the oxidizing process, some sulfide leaching occurred. For the calcite-saturated solution, the opposite trend was observed, namely K_d values were lower in the fresh Reducing Grout than in the Aged Reducing Grout. The cause for this is not clear.

The oxidizing and reducing cementitious K_d values used in past PA calculations are presented in (Table 3). These are literature K_d values that Kaplan (2006) took primarily from Bradbury and Sarott (1995) and Krupka and Serne (1998). There are no previous sorption experiments conducted with SRS cementitious materials. Most estimates of Reducing Grout

K_d values are based on very little laboratory data. Furthermore, it is commonly assumed that radionuclide sorption to reducing cementitious solids is the same as that of common oxidizing cementitious solids, except for those radionuclides that sorb more strongly in a reduced state, such as Np(V), Pa(V), Pu(IV), Tc(IV), and U(IV) (Bradbury and Sarott 1995, Krupka and Serne 1998). This was observed in the data (except for Pu). It is also commonly assumed that sorption in Stages 1 and 2 is generally greater than sorption in Stage 3 of cementitious solids (Bradbury and Sarott 1995, Krupka and Serne 1998). Again, this was the general trend.

A comparison of the measured K_d values to the literature K_d values (Kaplan 2006) presently used in the performance assessment is shown in Table 3. The measured K_d values were similar to the literature values for the Oxidizing Cementitious Solids/Stages 1 & 2, except for Cd, Cs, Pu, and Sr. For these exceptions, the measured K_d values were appreciably greater than the literature values. The literature K_d values for the Oxidizing Cementitious Solids/ Stage 3 are all consistently less than the measured values. The cause for this difference can be attributed to there being few experimental results of "aged" cements and therefore there is little information by which scientists can predict sorption at this stage. Also, as discussed above, the solid phase used to simulate Stage 3 (i.e., the Aged Cement in $CaCO_3$ solution) does not exactly match the conceptual environment believed by geochemist to exist in Stage 3. In Stage 3, the portlandite has been fully dissolved and the solubility or reactions of calcium-silicate-hydrate gel with the infiltrating water controls the water chemistry. The calcium-silicate-hydrate gel dissolves incongruently with a continual decrease in pH until it reaches the background pH, or pH 5.5. At the end of this stage, the 3rd Stage can be conceptualized as leaving only silica (SiO_2) as the solubility control for the pore water chemistry. Notably, the mineral assembly in the samples used for these measurements has not been weathered (aged) for thousands of years.

For the Reducing Cementitious Solids, literature K_d values were almost all less than those measured in this study, except for U and iodine. As was the case with the Oxidizing Cementitious Solids in the 3rd Stage, the literature K_d values for the Reducing Cementitious Solids in the 3rd Stage were less than the measured values. Again, the likely cause for this is: 1) the SRS reducing grout formulation is different than those previously used in sorption experiments (primarily the amount and type of slag used is unique), and 2) there has been an unwritten assumption that enhanced sorption to reducing cementitious solids is only due to favorable redox-induced transformations of the contaminant, and enhance sorption to the presence of sulfides were not considered.

K_d values measured in saturated $Ca(OH)_2$ (Stages 1 & 2) were all greater than those listed as Reducing Cementitious Solids in Stage III (Table 3). Finally, it needs to be reiterated that the experimental K_d results include absorption, adsorption, and precipitation. In some cases, such as the experiments using Am, Pa, U, Np, Sn, and Y, appreciable amounts of precipitation likely occurred.

In summary, the following general changes to the cementitious K_d values provided for SRS PAs (listed in Kaplan 2006) are supported by this study. An important underlying principle in making many of these suggested changes is that site-specific data is appreciably more accurate than literature data.

- Increase most Stage 1 & 2 values under oxidizing conditions to approximately the measured values. The only important exception is for U, which will be decreased from 1000 to 250 mL/g.
- Slightly increase all Stage 3 values, except U, under oxidizing and reducing conditions. As discussed above, the measured values were all appreciably greater than the literature values. The literature K_d values for Stage 3 were based on little experimental data. These measured values greatly increase the pool of existing literature reducing-grout K_d values, however, it needs to be kept in mind that the Stage 3 experimental conditions were such that they did not yield conservative K_d estimates.
- Increase most of the Stage 1 & 2 values under reducing conditions. This is to account for the sorptive capacity provide by sulfide bonding. Sorption values for iodine will not be changed, and those for Cs and U will be moderately reduced.

These recommended changes are presented in Table 4. Appendix A includes the integration of the data generated from this study into the K_d look-up tables for all 56 radionuclides modeled by the PA. In creating the K_d look-up tables a number of considerations are made and are presented in Kaplan (2006). Among the most important of these considerations is that site-specific K_d values are weighed more than literature values, the extent that experimental conditions producing literature K_d values simulate the SRS scenario of interest, and to maintain the various K_d values in the tables self consistent and consistent with well known chemical principles.

Table 2. K_d values appropriate for young ($Ca(OH)_2$) and old ($CaCO_3$) cementitious materials (mean and standard deviation of triplicate measurements; units = mL/g).

	Aged Cement - K_d				Aged Reducing Grout-K_d				Reducing Grout K_d			
	$Ca(OH)_2$		$CaCO_3$		$Ca(OH)_2$		$CaCO_3$		$Ca(OH)_2$		$CaCO_3$	
	avg	stdev	avg	stdev	avg	stdev	avg	stdev	avg	stdev	avg	stdev
Am(III)	6031	2145	4112	3742	(e)		40086	10088	42,887	29,994	17,113	19,602
Cd(II)	9907	3685	3180	1445			7565	1754	297,300	5293	17,510	13,838
Ce(III)	6003	2014	4652	4552			21284	6888	103,840	112,245	4564	1776
Co(II)	4343	969	3994	2888			26266	14083	15,065	10,665	6539	3137
Cs(I)	21	5.4	17.6	4.1			73	10	-2.3(a)	0.7	15	2.2
Hg(II)	289	9.8	568	191			841	179	1173	328	1095	957
I(-I)	14.8	4.9	14.4	7.3	22.9	4.4	24	2.9	6.2	0.2	11	6.0
Np(V)(b)	1652	1101	1318	764	644.3	37.9	3265	3250	3949	565	2779	2000
Pa(V)(b)	1630	4.9	1074	303	1018	33	24,618	12,729	9890	4589	8049	6577
Pu(IV/V)(d)	99,736	64,565	92,216	61,082	113,371	11,430	63	12	5,760	1,348	11,055	2,277
Sn(IV)	3900	63	3360	2579			7433	30	71,762	8983	5520	4015
Sr(II)	28.1	2.8	39.1	4.2			188	19	2.9	0.3	54.6	9.9
Tc(-VII) (b)	0.8	1.2	1.4	5.8	7.0	0.3	4.9	0.1	3910(c)	454(c)	940(c)	149(c)
U(VI) (b)	259	189	165	67	83.1	2.3	333.3	98.6	2489	2354	3182	2704
Y(III)	4830	1230	4738	4596			15920	5012	64,821	75,544	5336	2411

(a) For these experiments, negative K_d values should be assumed to be equal to 0 mL/g, and are likely attributed to analytical error.

(b) Np(V), Pa(V), Tc(VII) and U(VI) were added as NpO_2^+, PaO_2^+, TcO_4^-, and UO_2^{2+} respectively.

(c) Tc Kd measurements in reducing grout had to be redone because O_2 had entered the experimental system, thereby compromising the value of the data.

(d) Pu was added as Pu(V) but very likely converted to Pu(IV) via surface enhanced reduction.

(e) Empty cells indicate that no measurement was made.

Table 3. Comparison of the measured K_d values to the literature K_d values (Kaplan 2006) presently used in the performance assessment (units = mL/g).

	Oxidizing Cementitious Solids				**Reducing Cementitious Solids**			
	Stages 1 & 2		**Stage 3**		**Stages 1 & 2**		**Stage 3**	
	Kaplan (2006) (b)	**Measured(e)**	**Kaplan (2006) (b)**	**Measured(e)**	**Kaplan (2006) (b)**	**Measured(e)**	**Kaplan (2006) (b)**	**Measured(e)**
Am(III)	5000	6031	500	4112	5000	42,887	500	17,113
Cd(II)	500	9907	250	3180	500	297,300	250	17,510
Ce(III)	5000	6003	500	4652	5000	103,840	500	4564
Co(II)	1000	4343	500	3994	1000	15,065	500	6539
Cs(I)	2 – 4 (a)	21	2	17.6	2 – 4 (a)	-2.3 (c)	2	15
Hg(II)	500	289	250	568	500	1173	250	1095
I(-I)	8-20	14.8	0	14.4	8-20	6.2	0	11
Np(V) (d)	2000	1652	200	1318	2000	3949	200	2779
Pa(V) (d)	2000	1630	200	1074	2000	9890	200	8049
Pu(IV/V)	5000	99,700	500	92,200	5000	5,760	500	11,055
Sn(IV)	4000	3900	2000	3360	4000	71,762	2000	5520
Sr(II)	0.2 – 0.5 (a)	28.1	0.8	39.1	0.2 – 0.5 (a)	2.9	0.8	54.6
Tc(-VII) (d)	0	0.8	0	1.4	5000	NA	5000	NA
U(VI) (d)	1000	259	70	165	5000	2489	5000	3182
Y(III)	5000	4830	500	4738	5000	64,821	500	5336

(a) Ranges of Kd values exist where the proposed Kd values in Stage 1 differ from those in Stage 2. All single Kd entries indicate that the Kd values for Stages 1 and 2 are the same.

(b) Kd values for Oxidizing Cementitious Solids are the "Best" estimates for Stage 3 taken from Table 13 in Kaplan (2006). Kd values for Reducing Cementitious Solids are the "Best" estimates for Stages 1&2 taken from Table 14 in Kaplan (2006).

(c) For these experiments, negative Kd values should be assumed to be equal to 0 mL/g, and are likely attributed to analytical error.

(d) Np(V), Pa(V), Tc(VII) and U(VI) were added as NpO2+, PaO2+, TcO4-, and UO22+ respectively.

(e) Measure Oxidized Cement Stage 1 & 2 = Aged Cement/$Ca(OH)_2$ solution. Measure Oxidized Cement Stage 3 = Aged Cement/$CaCO_3$ solution. Measure Reducing Cement Stage 1 & 2 = Reducing Grout/$Ca(OH)_2$ solution. Measure Reducing Cement Stage 1 & 2 = Aged Cement/ $CaCO_3$ solution.

Table 1. Comparison of new (this report) and old (Kaplan 2006) "Best Estimate" values (units = mL/g).

	Oxidizing Cementitious Solids				**Reducing Cementitious Solids**			
	Stages 1 & 2		**Stage 3**		**Stages 1 & 2**		**Stage 3**	
	Kaplan (2006) (b)	**Recommended "Best" Estimate using this report's data**	**Kaplan (2006) (b)**	**Recommended "Best" Estimate using this report's data**	**Kaplan (2006) (b)**	**Recommended "Best" Estimate using this report's data**	**Kaplan (2006) (b)**	**Recommended "Best" Estimate using this report's data**
Am(III)	5000	6000	500	600	5000	5000	500	1000
Cd(II)	500	5000	250	500	500	5000	250	1000
Ce(III)	5000	6000	500	600	5000	5000	500	1000
Co(II)	1000	4000	500	1000	1000	5000	500	1000
Cs(I)	2 – 4 (a)	2 – 20	2	10	2 – 4	0 – 2	2	10
Hg(II)	500	300	250	300	500	1000	250	300
I(-I)	8-20	8 – 15	0	4	8 – 20	2 – 10	0	4
Np(V) (c)	2000	1600	200	250	2000	3000	200	300
Pa(V) (c)	2000	1600	200	250	2000	5000	200	500
Pu(IV/V)	5000	10,000	500	1000	5000	4000	500	500
Sn(IV)	4000	4000	2000	2000	4000	5000	2000	2000
Sr(II)	0.2 – 0.5	3 – 30	0.8	15	0.2 – 0.5	0.5 – 3.0	0.8	20
Tc(-VII) (c)	0	0.8	0	0.5	5000	NA	5000	NA
U(VI) (c)	1000	250	70	70	5000	2500	5000	2500
Y(III)	5000	5000	500	500	5000	5000	500	1000

(a) Ranges of K_d values exist where the proposed K_d values in Stage 1 differ from those in Stage 2. All single K_d entries indicate that the K_d values for Stages 1 and 2 are the same.

(b) K_d values for Oxidizing Cementitious Solids are the "Best" estimates for Stage 3 taken from Table 13 in Kaplan (2006). K_d values for Reducing Cementitious Solids are the "Best" estimates for Stages 1&2 taken from Table 14 in Kaplan (2006).

(c) Np(V), Pa(V), Tc(VII) and U(VI) were added as NpO_2^+, PaO_2^+, TcO_4^-, and UO_2^{2+} respectively.

4.2 APPROACH TO EQUILIBRIUM STUDY

The objective of this task was to measure the (ad)sorption kinetics of Am, Cd, Co, Ce, Hg, Sn, Sr, Cs, and Y. The intent of this work was to determine if the assumption of "instantaneous sorption" used in the performance assessment is correct. This assumption is implicitly made when K_d values are used.

4.2.1 Aged Cement

Figure 1 shows the change in radionuclide concentrations as a function of time, i.e., the approach of the solid/liquid/radionuclide system to equilibrium. Six measurements were made of the aqueous phase during the first 24 hr and a 7th measurement was made after 168 hr (1 week) of contact. After 24 hr, >99% of the various radionuclides had been sorbed by the Aged Cement (Table 5). Consequently, the difference between the amount of each radionuclides sorbed after 24 hr and 168 hr was very little, <1%. The K_d for these solutions were estimated by measuring the concentrations on the solid and the aqueous phases, as described in Equation 2. The changes in K_d values between these two contact times is considerably greater than would be expected for only a <1% change in aqueous radionuclide concentrations (Table 5). This apparent inconsistency may be attributed to: 1) very large K_d values being determined from analytical results close to the detection limit, and 2) to both the aqueous and solid phases concentrations changing between each contact time. It is not clear how to interpret the negative percent different K_d values, i.e., are they the result of radionuclide desorption between 24 and 168 hr, or the result of analytical noise. The calculated K_d values are extremely sensitive to the measured aqueous concentrations.

All the K_d values are plotted as a function of contact time in Figure 6 and Figure 8. The aqueous concentration suggests the system had reached steady state in 24 hr, but the K_d data suggests that only four (Am, Co, Sn and Sr) of the nine radionuclides had come to steady state. The implication is that contact times need to be longer than 24 hours for Cement K_d measurements. The steady state K_d values discussed in Section 4.1 had contact times of 1 week (Am, Cd, Co, Ce, Cs, Hg, Sn, Sr, and Y) or 2 weeks (I, Np, Pa, Pu, Tc and U).

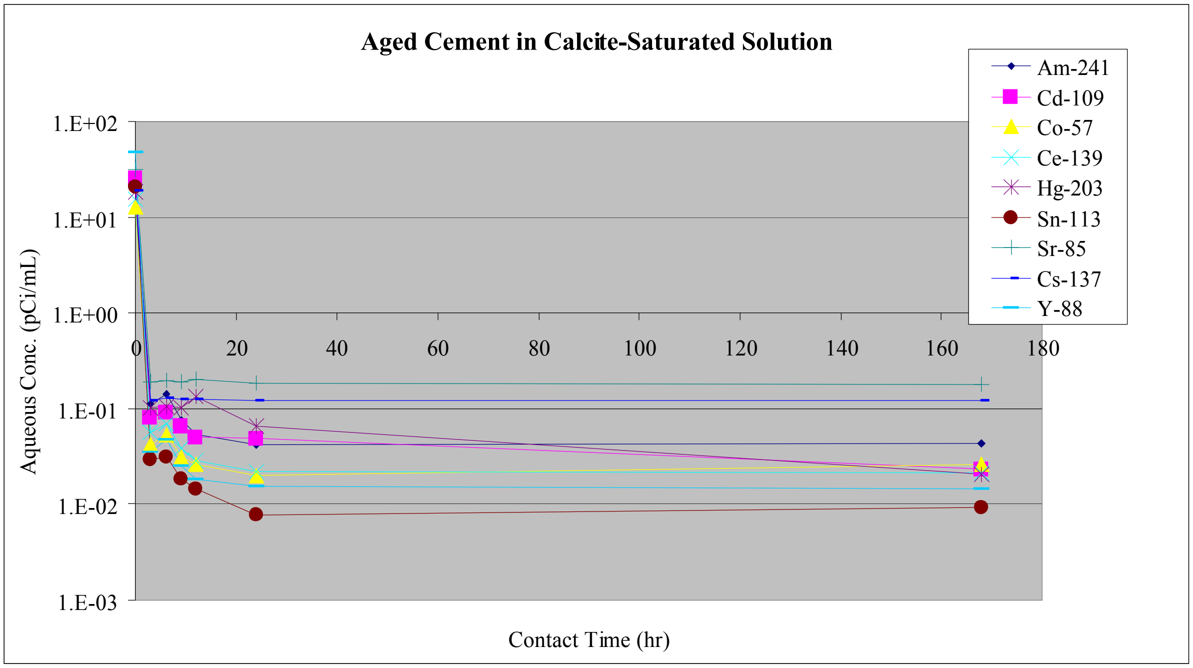
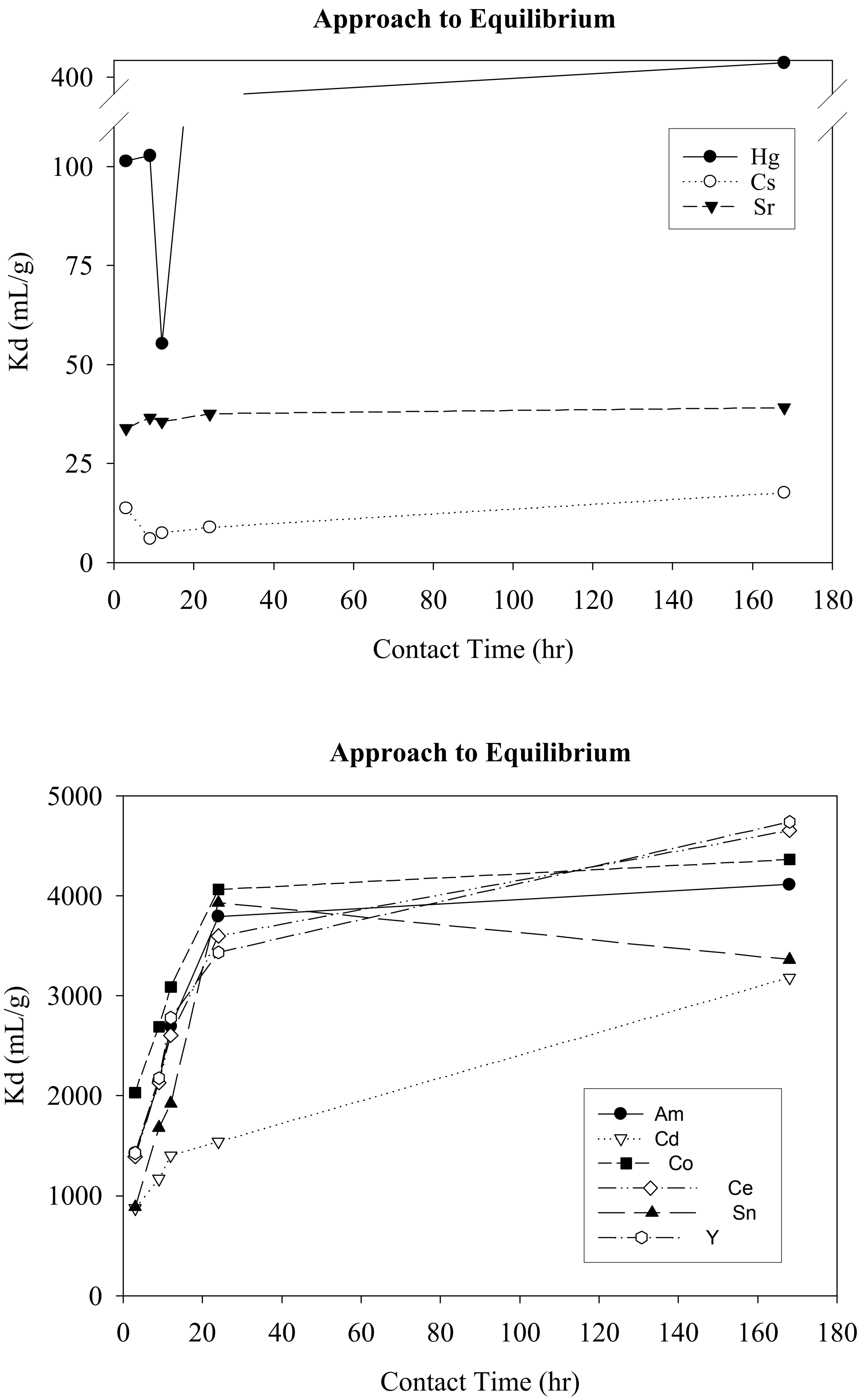


Figure 1. Aqueous radionuclide concentrations approach to equilibrium Aged Cement/calcite-saturated solution systems.

Table 5. Percent of radionuclide removed from the aqueous phase and percent change in K_d values between 24 hr and 168 hr contact time (Aged Cement and calcite-saturated solution).

	% Aqueous Removed			K_d		
	24 hr	168 hr	% Diff[(a)]	24 hr	168 hr	% Diff[(a)]
Am-241	99.810	99.800	-0.01	3793	4112	8.4
Cd-109	99.811	99.909	0.10	1539	3180	107
Co-57	99.845	99.793	-0.05	4061	4361	7.4
Ce-139	99.862	99.866	0.00	3597	4651	29
Hg-203	99.643	99.888	0.25	177	568	221
Sn-113	99.963	99.956	-0.01	3929	3360	-14
Sr-85	99.404	99.414	0.01	38	39	4.0
Cs-137	99.340	99.349	0.01	8.9	17.6	98
Y-88	99.968	99.970	0.00	3432	4738	38

(a) Percent difference with respect to the 24 hr contact time measurement.


Approach to Equilibrium

Approach to Equilibrium

Figure 2. Change in radionuclide K_d values as a function of contact time (Aged Cement in the calcite-saturated solution).

4.2.2 Reducing Grout

The results from the approach to equilibrium using Reducing Grout (section 4.2.1) were similar to those using the Aged Cement (Figure 1; Table 6). Greater than 99% of the aqueous radionuclide was removed within 24 hr contact time (Table 6). For five of the nine radionuclides, >99.9 % of the radionuclide was sorbed within the 24 hr contact period. Based on the K_d values (Table 6), five on the eight K_d values showed little change between 24 and 168 hr of contact. Again, one of the conclusions based on the K_d data is that batch sorption studies with cementitious materials require a greater duration to come to equilibrium than other materials, such as soils and sediments.

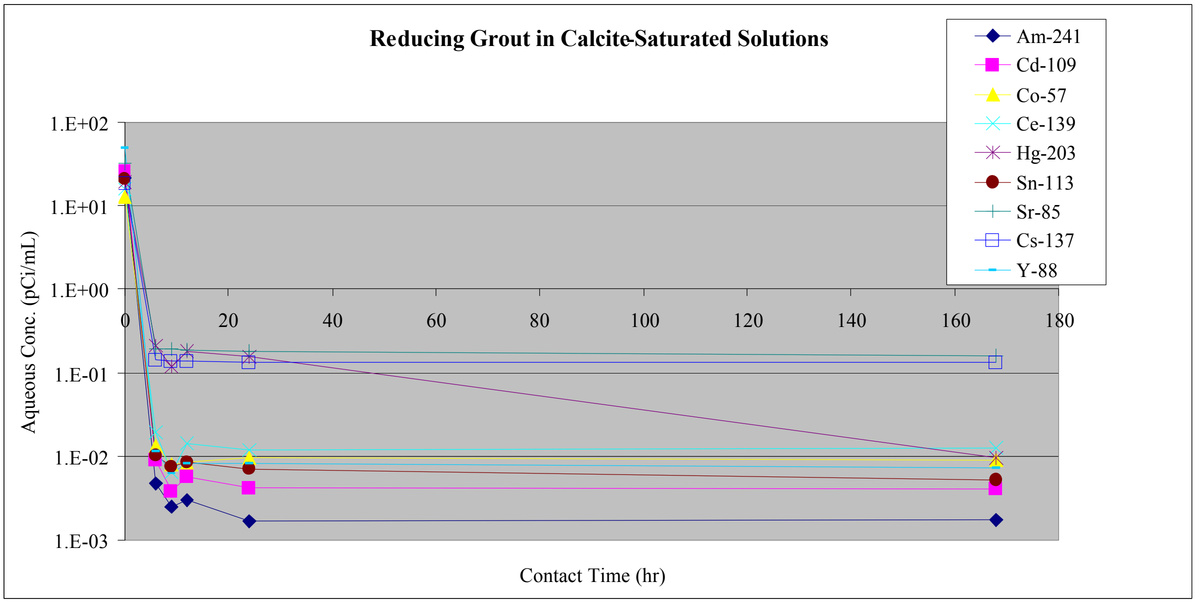


Figure 3. Approach to equilibrium of aqueous radionuclide concentrations of Aged Cement in a calcite-saturated solution.

Table 6. Percent of radionuclide removed from the aqueous phase and percent change in K_d values between 24 hr and 168 hr contact time (Reducing Grout and calcite-saturated solution).

	% Aqueous Removed			K_d		
	24 hr	168 hr	% Diff[(a)]	24 hr	168 hr	% Diff[(a)]
Am-241	99.992	99.992	0.00	43412	30262	30.3
Cd-109	99.984	99.981	0.00	28209	22860	19.0
Co-57	99.929	99.958	-0.03	6181	5978	3.3
Ce-139	99.920	99.942	-0.02	6255	5409	13.5
Hg-203	99.950	99.957	-0.01	NA	NA	NA
Sn-113	99.975	99.976	0.00	3678	4599	-25.0
Sr-85	99.491	99.261	0.23	50	52	-4.2
Cs-137	99.290	99.392	-0.10	12	13	-9.7
Y-88	99.985	99.967	0.02	5480	5408	1.3

(a) Percent difference with respect to the 24 hr contact time measurement.

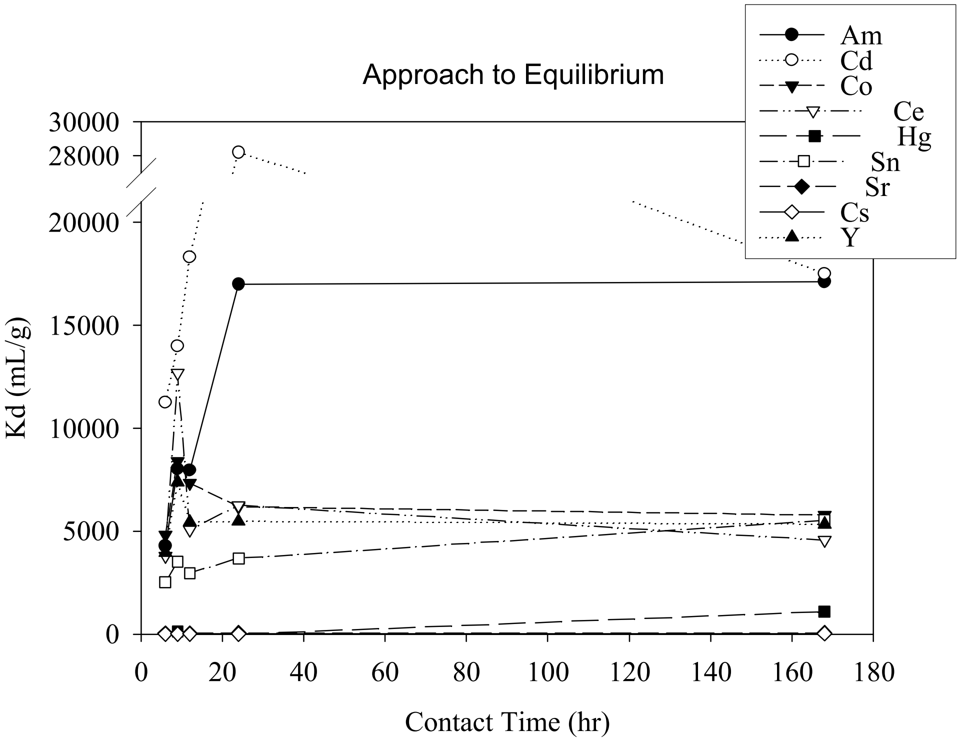


Figure 4. Change in radionuclide K_d values as a function of contact time (Reducing Grout in the calcite-saturated solution).

4.3 DESORPTION STUDY

The objective of this task was to determine if radionuclide desorption is reversible. In the context of a chemical reaction, this means that the rate of adsorption is equal to the rate of desorption. Another important objective of this work was to measure desorption kinetics. If the desorption rate is in fact slow, it may be more accurate to describe it with a kinetic term, rather than a steady state term, such as a K_d value. Our approach to this aspect of the study was to add aqueous radionuclides to crushed Aged Cement during a 7-day contact period. The radionuclide-spiked Aged Cement was packed in a small column and the column placed directly on a gamma counter. Influent and effluent lines were hooked up to the column and calcite-saturated water was slowly passed through the column. The flow rate was still greater than that anticipated in E-Area, but it provided a bounding condition for the greatest amount of radionuclide desorption. Desorption was enhanced because the high flow rates (with respect to groundwater) would maintain the aqueous radionuclide concentrations low, promoting the solid phase radionuclides to desorb.

4.3.1 Aged Cement – Desorption

The concentration of radionuclides sorbed to the crushed Aged Cement as a function of leaching duration is presented in Figure 5. The relative solid phase concentrations between the radionuclides do not in themselves provide much information. The amount on the solid phase is a function not only of how strongly the solid phase sorbed the radionuclides, but also of how much radionuclide was added in the initial gamma-spike cocktail. Therefore, attention should be directed at the change in sorbed radionuclide concentration.

The first observation that can be readily made is that desorption is very slow and certainly much slower than the (ad)sorption rates (Figure 3). Also, at first glance it appears that there is little change in solid phase radionuclide concentrations as a function of leaching duration, perhaps with the exception of Sr. However, upon closer examination of the data, some poignant trends can be discerned (Figure 6). Highly significant correlation coefficients (R^2) to either first or second order kinetic models were fitted to each radionuclide, except Am (Table 7).

The implications of these results are as follow.

- The PA is being conservative in its geochemical treatment of radionuclide interaction with cement. By using K_d values we assume that desorption occurs instantaneously, which this data shows is not the case.
- Should the PA need to be more accurate or less conservative, it may be appropriate to assume (ad)sorption occurs via K_d/solubility limits and desorption occurs via kinetic terms identified in Table 7.
- In the case of Am, where no significant correlation is observed, the mean value could be used to represent the steady release of radionuclides at a fixed rate; perhaps controlled by extremely slow kinetics or solubility limits.

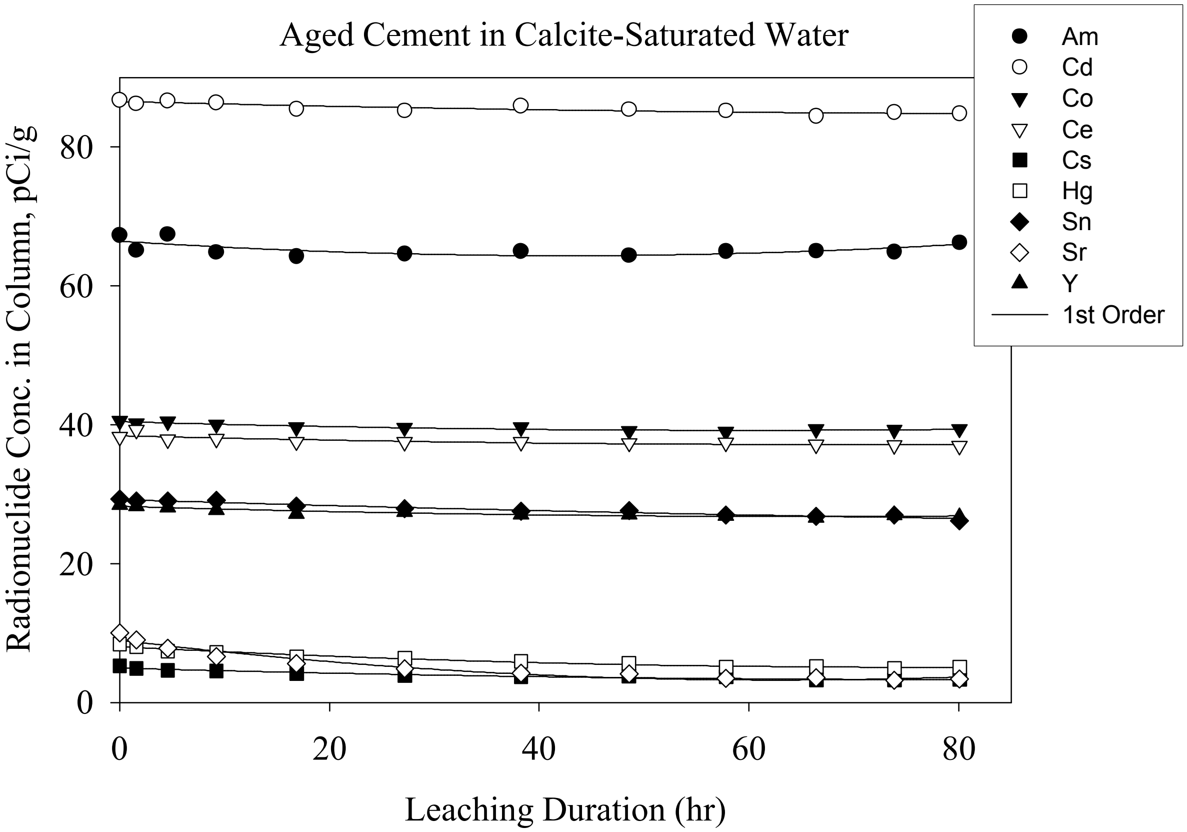


Figure 5. Radionuclide concentration remaining in a column of crushed Aged Cement as calcite-saturated water is pumped through it.

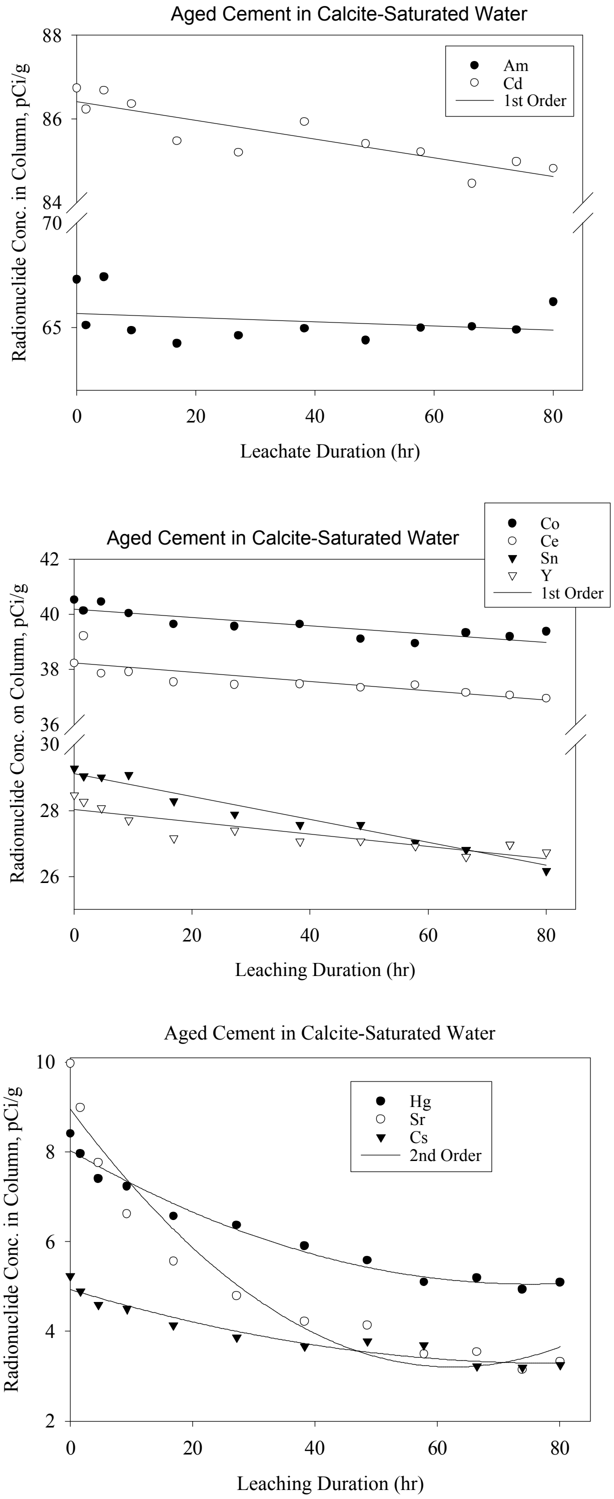


Figure 6. Desorption study showing the radionuclide concentration sorbed to Aged Cement as a function of leaching duration with a calcite-saturated water.

Table 7. Radionuclide desorption kinetics from crushed Aged Cement (radionuclides were initially sorbed onto the Aged Cement for 1 week before calcite-saturated solutions were used for leaching; units pCi/g; 12 observations).

	Am-241	**Cd-109**	**Co-57**	**Ce-139**	**Hg**	**Sn-113**	**Sr-85**	**Cs-137**	**Y-88**
Regression Order Fit	None[c]	1st	1st	1st	1st	1st	2nd	2nd	2nd
R^2	0.076	0.771	0.727	0.657	0.968	0.957	0.902	0.910	0.797
Significance[a]	NS	≤0.001	≤0.001	≤0.001	≤0.001	≤0.001	≤0.001	≤0.001	≤0.001
Intercept[b]		86.4	40.192	38.227	29.1099	3.37147	2.07985	1.56403	28.022
Slope[b]		-0.0224	-0.0151	-0.0168	-0.0346	-0.0012	-0.0130	-0.0054	-0.0187
Mean	65.32	85.62	39.66	37.63	6.31	27.89	5.46	4.00	27.36

[a] Probability of making a type one error; NS = not significant.

[b] Regression lines using the intercept and slope are presented in Figure 6.

[c] No regression order is provided for non-significant regressions.

4.3.2 Reducing Grout – Desorption

Radionuclide desorption from the Reducing Grout is presented in Figure 7[4]. Again, upon first examination, the data appears to show a flat response, with the exception of Sr. Upon closer examination, the data appears to have a great deal more noise than the Aged Cement data (Figure 8). Additionally, there were only two radionuclides, Cs and Sr, that had significant correlation coefficients (Table 8). The cause for this difference with the Aged Cement is not known, but may in part be the result of generally lower radionuclide concentrations near the instrument's detection limit, resulting in more noise in the Reducing Grout system.

Using the same reasoning as described for the Aged Cement (Section 4.3.1), the implications of these finding are as follows.

- It would be more accurate and less conservative to use first-order desorption kinetic rates (Table 8) for Cs and Sr.
- For all other radionuclides, it would be best to describe desorption by a fixed value, such as a solubility value (Table 8).

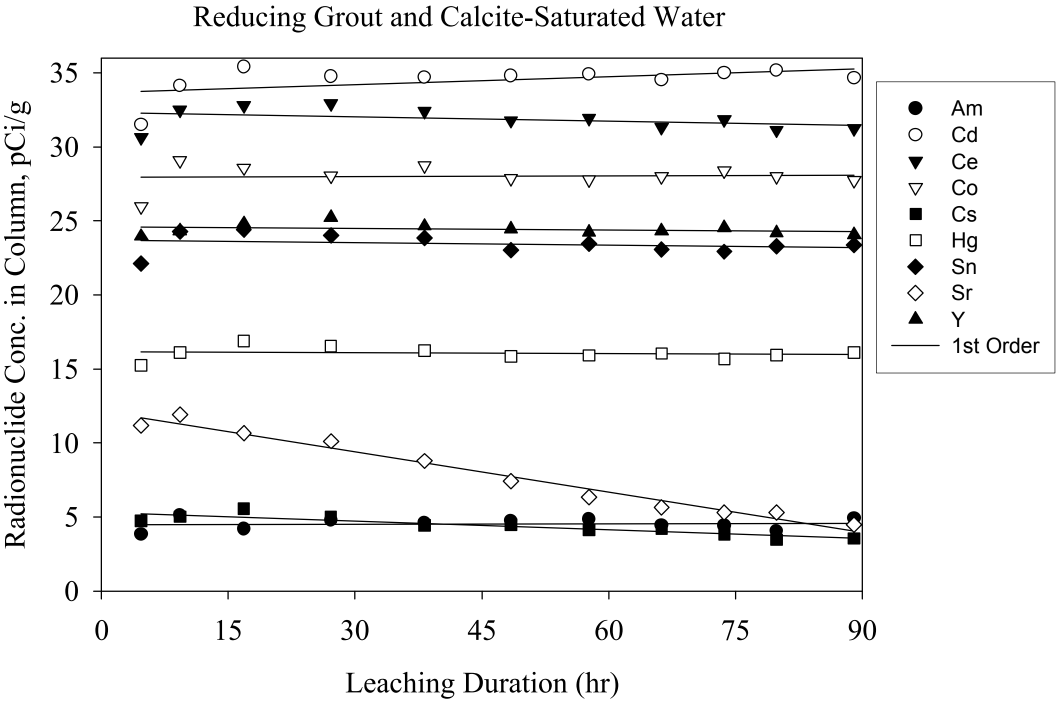


Figure 7. Radionuclide concentration remaining in a column of crushed Reducing Grout as oxidized, calcite-saturated water is passed through it.

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[4] The data from the first leaching duration, 0 hours, was not included in this figure (and all subsequent calculations and discussions) because there was clearly some unknown problem associated with this analysis; the concentrations at time equals zero for each radionuclide was much lower than the rest of their respective data sets.

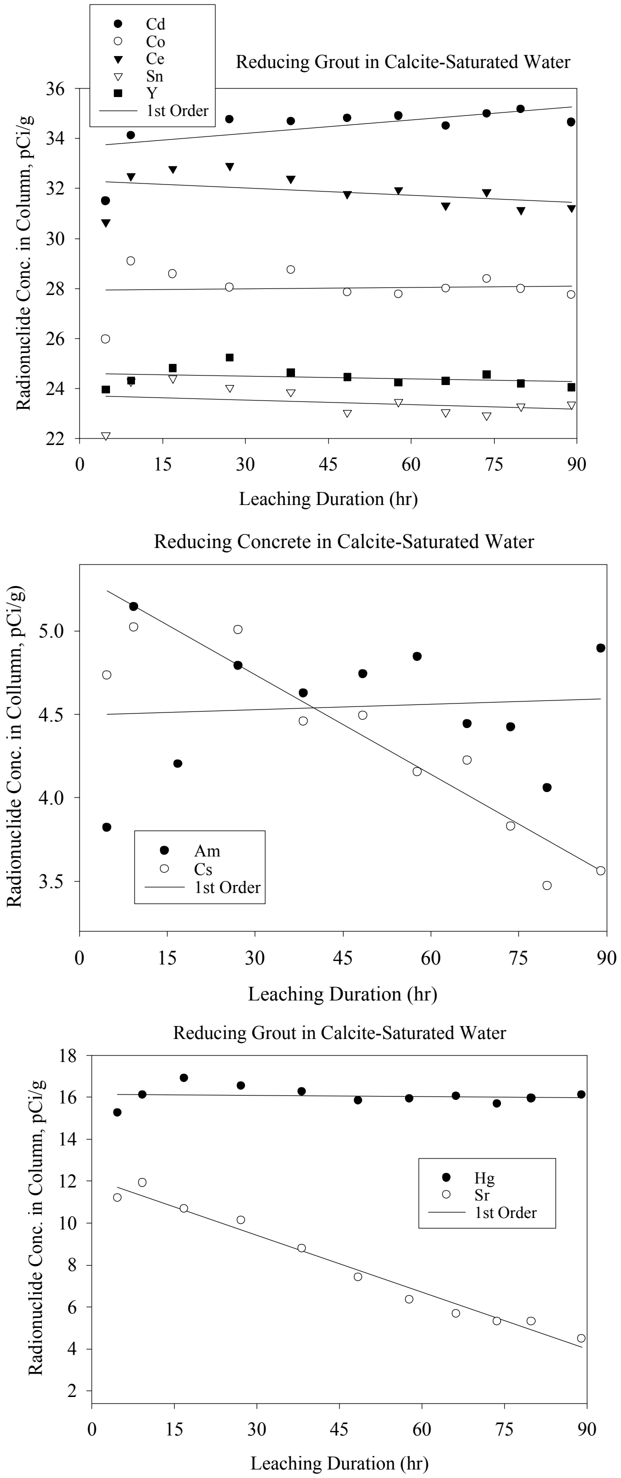

Figure 8. Desorption study showing the natural logarithm of radionuclide concentration sorbed on reducing grout in calcite-saturated water as a function of time.

Table 8. Desorption of radionuclides (ad)sorbed to crushed Reducing Grout for a week followed by leaching with calcite-saturated solution (Units pCi/g; 10 observations)

	Am-241	**Cd-109**	**Co-57**	**Ce-139**	**Hg**	**Sn-113**	**Sr-85**	**Cs-137**	**Y-88**
Regression Order Fit	None(c)	None	None	None	None	None	1st	1st	None
R^2	0.007	0.247	0.005	0.161	0.020	0.067	0.974	0.813	0.075
Significance(a)	NS	NS	NS	NS	NS	NS	0.001	0.01	NS
Intercept(b)							12.15	5.34	
Slope(b)							-0.0908	-0.0199	
Mean	1.516	3.550	3.336	3.465	2.774	3.151	1.853	1.411	3.196

(a) Probability of making a type one error; NS = not significant.

(b) Regression lines using the intercept and slope are presented in Figure 8.

(c) No regression order is listed for regression analyses that were not significant.

4.4 INFLUENCE OF REDUCING GROUT ON AQUEOUS CHEMISTRY

The objective of this task was to determine how long it takes for reducing grout to change the aqueous environment. Two separate small experiments were conducted. In the first, several water chemistry parameters were measured after a two week equilibration period. This was to provide a measure of what water conditions were at steady state. In the second study, pH, Eh (redox status), and electrical conductivity was measured as a function of contact time with Reducing Grout.

The results from the steady state experiment are presented in (Table 9). The water samples were analyzed for anions by ion chromatograph, cations by inductively coupled plasma – emission spectroscopy, total inorganic carbon with an infrared carbon analyzer and pH, Eh and electrical conductivity (an indirect measure of total dissolved salts) by their respective probes. Compare to the Aged Cement, the Reducing Grout had lower pH, Eh, and electrical conductivity levels and Ca, K, Na, and Sr concentrations. Conversely, compared to the Aged Cement, the Reducing Grout had greater Fe, Mg, S, and Si concentrations. The lower redox status of the Reducing Grout as compared to the Aged Cement is reflected in the lower Eh value. Reducing conditions are created by Reducing Grout by sulfides and ferrous iron. In the Aged Reducing Grout, the Eh is approximately the same as the Aged Cement, indicating it is oxidized, and it has much lower dissolved S and Fe concentrations compared to the Reducing Grout. The high electrical conductivity in the Aged Cement is largely the result of high concentrations of K and Na, both monovalent cations. Typically, these cations are much more abundant in young cement than in old cement samples. Perhaps, the high monovalent cation concentrations originated from evaporative salt formation.

Table 9. DDI water chemistry after being in contact with cementitious materials for two weeks.

	Aged Cement[a, b]	**Reducing Grout[a]**	**Aged Reducing Grout[a]**
pH (1:1; 1 hr contact)	11.99	11.16	11.24
Eh (SHE) (mV)	346.6	36.5	325.3
Electrical Cond. (dS/cm)	3.748	1.583	NA
B (mg/L)[c]	<0.126	0.264	1.01
Ca (mg/L)	183	122	45.0
Fe (mg/L)	<0.139	0.241	<0.139
K (mg/L)	238	74.7	23.0
Mg (mg/L)	0.455	4.46	7.29
Mn (mg/L)	<0.0480	0.049	0.099
Na (mg/L)	244	107	61.1
S (mg/L)	<5.93	227	35.4
SO_4^{2-} (mg/L)	<100	420	120
Si (mg/L)	1.44	24	15.5
Inorganic C (mg/L)	9.27	18.2	11.9
Sr (mg/L)	4.13	0.57	<0.209

(a) 10 g of solids + 25 mL of D.I. water, except Aged Reducing Grout where 6.1 g of solids + 25 mL of D.I. water were used. Study conducted on the bench top in closed glass containers. No effort was taken to eliminate oxygen from the system.

(b) Aggregate was removed and only cement used in this and all other tests described in this report.

(c) Cation analyses was by ICP-ES; anion analysis by ion chromatography (F^-, Cl^-, NO_3^-, Br^-, NO_2^-, and PO_4^{3-} had below detection concentrations)

The change in aqueous chemistry in a Reducing Grout/DDI-water system is presented in Figure 9. pH and electrical conductivity came to equilibrium within 0.5 hr. This finding is expected, since both measurements are typically taken of a solid/liquid suspension after only a 1-hr contact time. The Eh took 4 days to come to steady state. Lowering the redox status, or Eh, with Reducing Grout is a chemically complicated process, and as such is not expected to occur instantaneously, as was the case with pH and electrical conductivity. Slag, the redox active ingredient, creates a reducing environment with Fe^{2+} and sulfide. An important difference between the experimental set up for the data presented in Figure 9 and that presented in Table 9 is that the former was conducted with a N_2 atmosphere, whereas the latter was conducted in air, with no attempt to reduce the presence of $O_2(g)$.

The key result from this research is that Reducing Grout can create a reducing environment in extremely short period of time, 4 hr. There are few, if any, scenarios in which the groundwater would be in contact with the Reducing Grout for <4 hr. Furthermore, the issue of whether it takes a long time for grout to create a reducing environment can be laid to rest. Four hours is essentially instantaneous in the timeframes that are relevant to the PA.

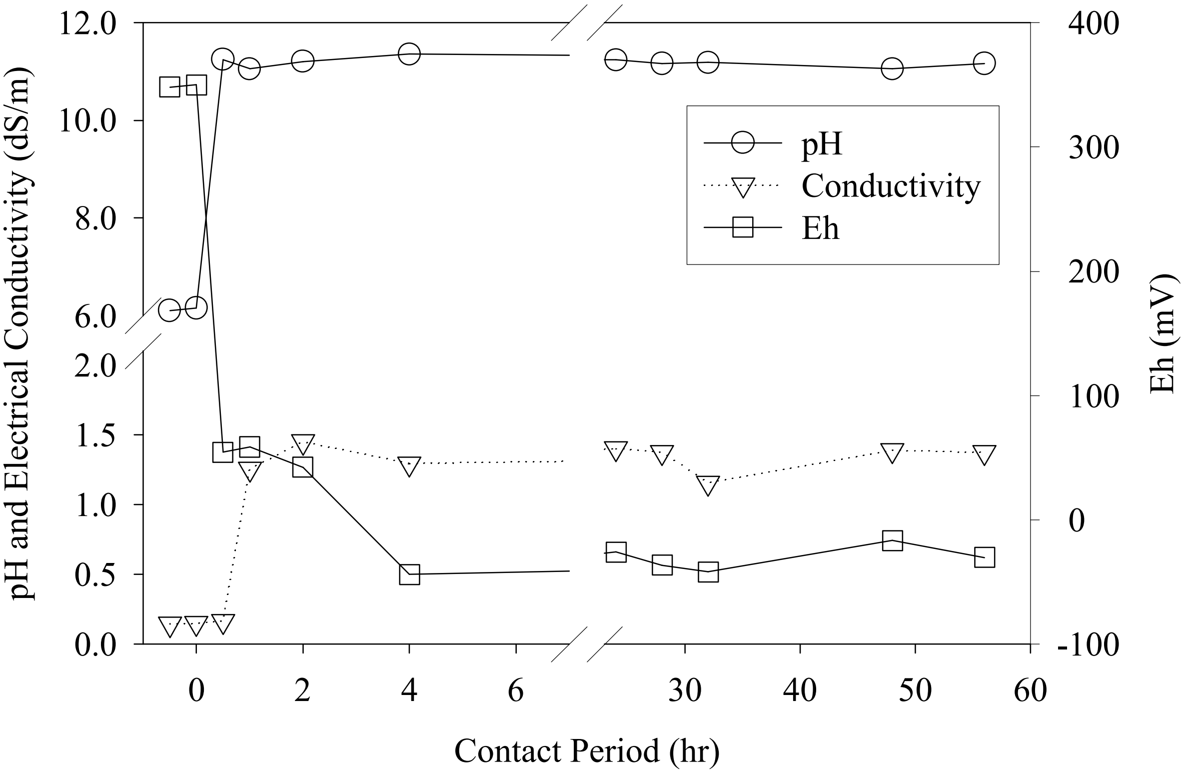

Figure 9. Change in aqueous chemistry as a function of contact time with Reducing Grout (10g solid and 25 mL DDI water; N_2 atmosphere).

5.0 CONCLUSIONS

There were four separate studies conducted for this task: Batch Sorption Study, Approach to Equilibrium Study, Desorption Study, and Influence of Reducing Grout on Aqueous Chemistry Study. The first was to measure K_d values for use in the PA. This study measured K_d values for 15 radionuclides, three solids (Aged Cement, Reducing Grout, and Aged Reducing Grout), and two aqueous phases (portlandite-saturated solution to simulate leachate from a young cement, and a calcite-saturated solution to simulate leachate from an older cement). An important underlying principle in making many of these suggested changes is that site-specific data is appreciably more reliable than literature data. A list of these general findings is below.

- Increase most Stage 1 & 2 (young and moderately aged cement) K_d values under oxidizing conditions to approximately the measured values. The only important exception is for U, which should be decreased from 1000 to 250 mL/g.

- Slightly increase all Stage 3 (aged cement) K_d values, except U, under oxidizing and reducing conditions. As discussed above, the measured values were all appreciably greater than the literature values, except U in Stage 3. Past literature K_d estimates for Stage 3 were based on little experimental data. These measured values will greatly increase the pool of existing literature relevant to Reducing Grout K_d values.
- Increase most of the Stage 1 & 2 values under reducing conditions. This is to account for the sorptive capacity provide by sulfide bonding. Sorption values for iodine will not be changed, and those for Cs and U will be moderately reduced.

The main conclusion from the Approach to Equilibrium study was that all radionuclides evaluated approach equilibrium very quickly, between a day and a week. This is important because it is an implicate assumption when using the K_d construct.

One of the main objectives of the Desorption Study was to evaluate whether (ad)sorption and desorption rates were similar, which is also assumed when using the K_d construct. Desorption rates were much slower than (ad)sorption rates. More specifically, the implications of the Desorption Study are as follows.

- The PA is being conservative in its geochemical treatment of radionuclide interaction with cementitious materials. By using K_d values we assume that desorption occurs instantaneously, which this data shows is not the case.
- Should the PA need to be more accurate or less conservative, it may be appropriate to assume adsorption occurs via K_d/solubility limits and desorption occurs via kinetic terms identified in Table 7.

In the study about Reducing Grout's Influence on Aqueous Chemistry, it was demonstrated that Reducing Grout can create a strongly reducing environment in a very short period of time, 4 hrs. There are few, if any, PA scenarios in which the groundwater would be in contact with the Reducing Grout for <4 hr. Furthermore, the issue of whether it takes a long time for grout to create a reducing environment can be laid to rest. Four hours is essentially instantaneous in the timeframes relevant to the PA.

6.0 APPENDIX A: RECOMMENDED KD VALUES FOR USE IN FUTURE PERFORMANCE ASSESSMENT CALCULATIONS

Table 10. Distribution coefficients (K_d values, mL/g): Oxidizing Cementitious Solids

Radio-nuclide	**Young Cement 1st Stage (pH ~12.5)**		**Moderately-aged Cement, 2nd Stage (pH ~10.5)**		**Aged Cement (b) 3rd Stage (pH ~5.5)**		
	Conser-vative	**"Best"**	**Conser-vative**	**"Best"**	**Conser-vative**	**"Best"**	**Comments/References(a)**
Ar, Kr, Rn, N	0	0	0	0	0	0	CrO_4^{2-} (an anion analogue) immobilization as a result of carbonation (the natural process by which concrete becomes coated with $CaCO_3$) has been documented (*5*). Until studies are conducted to prove otherwise (such as tritium (see below), it will be necessary to assume their *Kd* values = 0 mL/g.
^3H	0	0	0	0	0	0	A great deal of recent research has been conducted using careful measurements of tritium sorption to cement (reviewed by Wieland and Van Loon 2003 and Tits et al. 2003). Through the use of batch sorption and through-diffusion experiments they have arrived at essentially the same *Kd* value, 0.8 ± 0.2 mL/g and 0.8 ± 0.1 mL/g, respectively. In Wieland and Van Loon's (2003) look-up table for cement *Kd* values, they suggest using a value of 1 mL/g for tritium (this value would be equivalent to a "Best" value in this table). However, there is also a great deal of data indicating that tritium really doesn't sorb and that experimental evidence indicating so is, in some cases, actually errors in mass balance (reviewed by Krupka et al. 2004). That is, during diffusion tests or batch sorption test, researchers incorrectly assign tritium existing in the concrete/cement pore water as "sorbed tritium" during their mass balance calculations (*Kd* calculations).
Ac, Am, Bk, Cf, Cm, Eu, Fe(III), Gd, Sm, Al	3000	6000	3000	6000	400	600	Trivalent cation *Kd* values for concrete exceed those for sediments (3). Am *Kd* > 10,000 mL/g (*10*). Am *Kd* value was 12,000 mL/g based on diffusion tests in cement (*11*). Am *Kd* values ranged from 2,500 to 35,000 mL/g for 7 fresh concrete blends (*1, 6*). Am *Kd* for 65-yr old concrete sample = 10,000 mL/g (*1, 6*). Fresh cement Am *Kd* = 2000 for 24-h contact time (*12*). Eu *Kd* = 2,400 mL/g for 24-h contact time (*12*). Very large *Kd* values may reflect precipitation reaction that occurred during the adsorption measurements. Kaplan and Coates (*24*) measured Am(III), Ce(III), and Y(III) *Kd* values for a 50-yr old SRS concrete sample using two leachate simulants for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (sat.-$CaCO_3$ solution). *Kd* values for the Stages 1&2 and Stage 3 were respectively, 6031 and 4112 mL/g for Am(III), 6003 and 4652 mL/g for Ce(III), and 4830 and 4738 mL/g Y(III).
Cl, Cr, F	2	20	2	20	0	2	Based on diffusion studies with French sulfate-resistant cement Cl *Kd* values

Radio-nuclide	**Young Cement 1st Stage (pH ~12.5)**		**Moderately-aged Cement, 2nd Stage (pH ~10.5)**		**Aged Cement (b) 3rd Stage (pH ~5.5)**		
	Conser-vative	**"Best"**	**Conser-vative**	**"Best"**	**Conser-vative**	**"Best"**	**Comments/References*(a)***
							were 25 mL/g (*2*). Atkins and Glasser (*3*) also reported Cl sorption to cement, but it was not possible to calculate a *Kd* based on the data provided in the paper. Cl *Kd* to cement powder after 24 h contact time = 0.8 mL/g (*4*). (This latter value is not especially reliable considering the experimental technique.) Decreased *Kd* values in "Young Concrete" because of high concentration of aqueous salts. In 1st Stage *Kd* values were decreased because high ionic strength likely resulted in anion exchange (desorption). Assume Cr exists as CrO_4^{2-}. K_d values taken from Bradbury and Sarott (*19*) for Cl.
Co, Cd, Ni, Pd, Zn	500	4000	500	4000	360	1000	Three studies were found that included adsorption data for Ni onto cement/concrete. Hietanen et al (*15*) reported *Kd* values that ranged from 500 to 3000 mL/g, Kato and Yanase (*12*) reported a Ni *Kd* value of 1500 mL/g, and Pilkington and Stone (*16*) reported *Kd* values that ranged from 500 to 3000 mL/g. Kaplan and Coates (*24*) measured Cd(II) and Co(II) *Kd* values for a 50-yr old SRS concrete sample using two leachate simulants for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution). The *Kd* values for the Stages 1&2 and Stage 3 were respectively, 9907 and 3180 mL/g Cd(II), and 4343 and 3994 mL/g Co(II).
Np, Pa	800	1600	800	1600	140	250	These radionuclides are assumed to exist in the +5 oxidation state. Np sorption test to 7 different 65-yr old cements using cement pore water reached steady state after 30 days, *Kd* values ranged from 1500 to 9500 mL/g (*1, 6*). As is the case with all large *Kd* values, these values may reflect some precipitation occurring during the adsorption measurement. Kaplan and Coates (*24*) measured Np(V) and Pa(V) *Kd* values for a 50-yr old SRS concrete sample using two leachate simulants for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution). The *Kd* values for the Stages 1&2 and Stage 3 were respectively, 1652 and 1318 mL/g Np(V) and 1630 and 1074 mL/g Pa(V).
Se, Te	100	300	210	300	110	150	Twenty-seven cementitious formulations (varying water/solid, silica fume %, and clay concentration) were used to measure selenate (SeO_3^{2-}) *Kd* values from an alkaline solution (Johnson et al. 2000). *Kd* values ranged from 250 to 930 mL/g. Sorption was irreversible. At high selenate (SeO_4^{2-}) concentrations, sorption to ettringite, monosulfate, calcium-silicate-hydrate (all mineral constituents of concrete) resulted in selenate substitutes for

Radio-nuclide	**Young Cement 1st Stage (pH ~12.5)**		**Moderately-aged Cement, 2nd Stage (pH ~10.5)**		**Aged Cement (b) 3rd Stage (pH ~5.5)**		
	Conser-vative	**"Best"**	**Conser-vative**	**"Best"**	**Conser -vative**	**"Best"**	**Comments/References[(a)]**
							sulfate (*23*). Selenite *Kd* values measured in sulfate resistant Portland cement ranged from 30 to 100 mL/g (Wieland and Van Loon 2003). It is not clear why these latter *Kd* values were so much lower than those reported by Johnson et al (2000). This variability in results requires that conservative values in table be lowered.
Pb, Po	250	500	250	500	180	250	Soft divalent cations: Bayliss et al. (1988) conducted a series of sorption experiments with Pb and crushed sulfate resisting Portland cement and ordinary Portland cement/blast furnace slag pastes with an Eh of +50 to -500 mV. The main findings were that sorption was concentration and cement composition dependent. Data strongly suggested solubility controls on Pb aqueous concentrations. "Best" estimates taken from (*19*).
Pu(III/IV), Pu(V/VI), Pu(combo) Th, Zr	1000	5000	1000	5000	250	500	Concrete containing reducing agents (blast furnace slag, BFS) did not have greater Pu *Kd* values than those that did not contain BFS. High *Kd* values are attributed more to low solubility of Pu in high pH systems, than to adsorption/absorption processes. Using three 65-yr-old crushed concrete samples and seven fresh concrete samples, Th-*Kd* values were 2,500 to 5,500 mL/g (*1, 6*). Th- *Kd* values were consistently less than Am *Kd* values, greater than U- *Kd* values, and very similar to Np and Pu *Kd* values (*1, 6*). Pu- *Kd* values ranged from 1,000 to 12,000 mL/g (*1, 6*). Using a sulfate resistant Portland cement, Th *Kd* values were measured to be 100,000 mL/g (*17*).
Cs, Fr, K, Rb	1	2	3	20	1	10	Cs *Kd* values in hardened HTS cement discs, pH 13.3 were close to 3 mL/g (*15*). Wieland and Van Loon (*17*) reviewed Cs *Kd* values onto various cementitious materials and they had a very narrow range: from 0.2 to 5.0 mL/g. In 1st Stage *Kd* values were decreased because high ionic strength likely results in competitive exchange (desorption). This has been shown experimentally (*17*). Kaplan and Coates (*24*) measured Cs *Kd* values for a 50-yr old SRS concrete sample using two leachate simulants for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution); the *Kd* values were 21.0 and 17.6 mL/g, respectively.
Ra, Ba	70	100	70	100	50	70	Bayliss et al. (*11*) and Berry et al. (*13*) measured Ra *Kd* values onto ordinary Portland cement and as a function of Ra concentration. They reported *Kd* values that ranged from 50 to 530 mL/g.

Radio-nuclide	**Young Cement 1st Stage (pH ~12.5)**		**Moderately-aged Cement, 2nd Stage (pH ~10.5)**		**Aged Cement (b) 3rd Stage (pH ~5.5)**		
	Conser-vative	**"Best"**	**Conser-vative**	**"Best"**	**Conser -vative**	**"Best"**	**Comments/References*(a)***
Sr	0.2	3	5	30	2	15	Jakubick et al. (*14*) reported Sr *Kd* values of 0.8 to 1.6 mL/g for high density and normal density concretes, and 1.3 to 3 mL/g for the same concretes, but in lower ionic strength solutions. Ewart et al. *(14*) reported *Kd* values between 1 and 4 mL/g. Kato and Yanase reported a Sr *Kd* value of 56 mL/g for an experiment involving 24 h contact time, dried cement powder, pH 11 cement equilibrated water. We elected to disregard this value because it is an order-of-magnitude greater than those reported by other researchers and the nature of the solid phase was not clearly described by the author. In 1st Stage *Kd* values were decreased because high ionic strength likely results in competitive exchange (desorption). Kaplan and Coates (*24*) measured Sr *Kd* values for a 50-yr old SRS concrete sample using two leachate simulants for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution); the *Kd* values were 28.1 and 39.1 mL/g, respectively.
I, At	6	8	10	15	0	4	I assumed to be present as iodide (I^-). Iodide sorbed stronger to cement than Cs (*1*). I- *Kd* measured on 7 types of concrete samples increased gradually over 3-mo, then leveled off at 25 to 130 mL/g (*1*, *6).* Iodide sorption to cement is highly reversible when Cl is added to aqueous phase, suggesting it adsorbed and was not precipitated (*3*). Increasing pH, decreased I^- sorption (*3;* therefore Stage 3 *Kd* values will be slightly greater than other stages). Iodide sorption on CSH varies with its C/S ratio, increasing towards high C/S ratios (*3*). Decreased *Kd* values in "Young Concrete" because of high concentration of aqueous salts. In 1st Stage *Kd* values were decreased because high ionic strength likely resulted in anion exchange (desorption). Kaplan and Coates (*24*) measured I^- *Kd* values for a 50-yr old SRS concrete sample using two leachate simulants for Stages 1&2 and Stage 3; the *Kd* values were 14.8 and 14.4 mL/g, respectively.
Tc, Re	0	0.8	0	0.8	0	0.5	TcO_4^- adsorption to cementitious material has been measured between 1 and 10 mL/g (*1*). Kaplan and Coates (*24*) measured TcO_4^- *Kd* values for a 50-yr old SRS concrete sample using two leachate simulants for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution); the *Kd* values were 0.8 and 1.4 mL/g, respectively.
Ag, Cu	0.1	1	0.1	1	0	0.1	Ag K_d values from Bradbury and Sarott (*19*).

Radio-nuclide	**Young Cement 1st Stage (pH ~12.5)**		**Moderately-aged Cement, 2nd Stage (pH ~10.5)**		**Aged Cement (b) 3rd Stage (pH ~5.5)**		
	Conser-vative	**"Best"**	**Conser-vative**	**"Best"**	**Conser-vative**	**"Best"**	**Comments/References(a)**
Hg	30	300	30	300	30	300	Kaplan and Coates (*24*) measured Hg(II) *Kd* values for a 50-yr old SRS concrete sample using two leachate simulants for Stages 1&2 (saturated Ca(OH)$_2$ solution) and Stage 3 (saturated-CaCO$_3$ solution); the *Kd* values were 289 and 568mL/g, respectively.
Inorganic C (c)	14	20	7	10	0	0	^{14}C chemistry is very complicated and is not well characterized by the *Kd* construct. It is influenced by carbon dioxide gas/water/solid phase equilibrium, isotopic exchange, adsorption, precipitation, and coprecipitation. To be conservative the role of gas phase and isotopic exchange (two very important processes for removing ^{14}C from groundwater) will not be considered. Inorganic C exists as an anion, CO$_3^{2-}$ (*1*). Subsurface C chemistry in a cementitious environment is discussed by Dayal (7, 8) and how it has been applied to the SRS by Kaplan (*9*).
Sn	2000	4000	2000	4000	1000	2000	Sn exists in cementitious environments in the +4 state (*17*) and as such readily hydrolyses. Using sulfate resistant Portand cement, Sn *Kd* values were >30,000 mL/g; this likely reflected some precipitation (*17*). Kaplan and Coates (*24*) measured Sn *Kd* values for a 50-yr old SRS concrete sample using two leachate simulants for Stages 1&2 and Stage 3; the *Kd* values were 3900 and 3360 mL/g, respectively.
Nb	500	1000	500	1000	360	500	Krupka and Serne (*18*) review Nb *Kd* values and concluded that there was a great deal of variability related in Nb sorption data to cementitious materials. They reported *Kd* ranges of 11 to 69,000 mL/g (from studies that had problems with the blanks, *i.e.*, the blanks indicated Nb sorbed to the glassware). We defer to their best values (1000 mL/g) and add conservatism to these values.
Sb	50	100	50	100	0	2	The literature indicates there have been very few Sb sorption studies conducted. Ames and Rai (*25*) reviewed Sb sorption and concluded that over the pH range of 4 to 8 that Sb exists as a neutral and complexed species. In high pH and high ionic strength systems, Sb K_d values were very low, 0 to 2 mL/g (Ames and Rai 1976). When Ca concentrations were high, such as in a concrete system, Sb appeared to coprecipitate with CaCO$_3$, yielding K_d values in the range of 17 to 122 mL/g. Beneath leaking high level waste tanks in Hanford, Sb was found to migrate rapidly through the subsurface sediment (at the same rate as Co and ruthenium) (*25*). The high mobility may be attributed

Radio-nuclide	**Young Cement 1st Stage (pH ~12.5)**		**Moderately-aged Cement, 2nd Stage (pH ~10.5)**		**Aged Cement [(b)] 3rd Stage (pH ~5.5)**		
	Conser-vative	**"Best"**	**Conser-vative**	**"Best"**	**Conser-vative**	**"Best"**	**Comments/References[(a)]**
							to the tendency of Sb to form complex or hydrolyzed species which are neutral or negatively charged.
Na	0	0.5	0	1	0	0.5	There has not been any Na sorption studies conducted with SRS sediments. Estimates were based on literature values. Because Na is highly hydrated, it tends to sorb weakly to sediments and concrete.
Mo	0	0.1	0	0.1	0	0.1	Mo(VI) as MnO_4^{2-} in oxidizing environ.; $CaMoO_4^0$ in cementitious environ.; Mo(IV) in reducing environ.
Mn	70	100	70	100	5	10	Mn K_d values from Bradbury and Sarott (*19*).
As	700	1000	700	1000	50	100	Phosphate, an analog for AsO_4^{3-}, is known to be strongly bound to concrete.
U	100	250	100	250	50	70	U(VI)- *Kd* values for 7 types of cement were 350 to 13,000 mL/g; median = 1400 mL/g (*1,6*). Kaplan and Coates (*24*) measured U(VI) *Kd* values for a 50-yr old SRS concrete sample using two leachate simulants for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution); the *Kd* values were 259 and 165 mL/g, respectively.

[(a)] References: (*1*) = Allard et al. 1984; (*2*) = Sarott et al. 1992 ; (*3*) = Atkins and Glasser 1992 ; (*4*) = Brodda 1988 ; (*5*) = Macias et al. 1997; (*6*) = Hoglund et al. 1985 ; (*7*) = Dayal and Reardon 1992; (*8*) = Dayal et al. 1989; (*9*) = Kaplan 2005; (*10*) = Ewart et al. 1988; (*11*) = Bayliss et al. 1991; (*12*) = Kato and Yanase 1993; (*14*) = Ewart et al. 1986; (*15*) = Sarott et al. 1992; (*16*) = Pilkington and Stone 1990; (*17*) = Wieland and Van Loon 2003; (*18*) = Krupka and Serne 1998; (*19*) = Bradbury and Sarott 1995; (*20*) = Tits et al. 2003; (*21*) = Krupka et al. 2004; (*22*) = Johnson et al. 2000; (*23*) = Baur and Johnson 2003; (*24*) = Kaplan and Coates 2007; (*25)* = Ames and Rai 1979.

[(b)] The age of each of the stages is facility specific because it depends on the amount of water that passes through the cementitious material (see Section 3.1.2).

[(c)] Inorganic carbon geochemistry is very complicated. The use of only the *Kd* value without the associated solubility value in a cementitious environment will greatly overestimate the true mobility of C through this environment.

Table 11. Distribution coefficients (K_d values, mL/g): Reducing Cementitious Solids

Radio-nuclide	**Young Cement 1st Stage (pH ~12.5)**		**Moderately-aged Cement 2nd Stage (pH ~10.5)**		**Aged Cement 3rd Stage (pH ~5.5)**		
	Conser-vative	**"Best"**	**Conser-vative**	**"Best"**	**Conser-vative**	**"Best"**	**Comments/References(a)**
^{3}H, Ag, Ar, As, Cl, Cu, ^{F,} Kr, Mn, Mo, N, Na, Nb, Inorganic C, Po, Pu(III/IV), Pu(V/VI), Pu(combo), Rn, Se, Th, Pb, Te, Zr	(Same values as reported in Table 10 for Oxidizing Cementitious Solids)						Concrete containing reducing agents (blast furnace slag, BFS) did not have greater Pu, Np, or Pa *Kd* values than those that did not contain BFS (*1, 2, 3*).
Ac, Al, Am, Bk, Cf, Cr, Cm, Eu, Gd, Sm, Sb	3000	5000	3000	5000	400	1000	Kaplan and Coates (*4*) measured Am, Ce, and Y *Kd* values for an SRS reducing grout containing 210 lbs/yd^3 of slag. They measured the *Kd* values in leachate simulates appropriate for Stages 1&2 (saturated Ca(OH)$_2$ solution) and Stage 3 (saturated-CaCO$_3$ solution). The *Kd* values for the Stages 1&2 and Stage 3 were respectively, 42,887 and 17,113 mL/g Am, 103,840 and 4564 mL/g Ce, and 64,821 and 5336 mL/g Y. They speculated that the presence of sulfides in the reducing grout were responsible for the strong sorption of these trivalent cations. It is assumed that Cr is in the lower redox state, i.e., Cr(III).
Cd, Co, Ni, Fe(II), Pd, Zn	1500	5000	1500	5000	500	1000	Kaplan and Coates (*4*) measured Cd and Co *Kd* values for an SRS reducing grout containing 210 lbs/yd^3 of slag. They measured the *Kd* values in leachate simulates appropriate for Stages 1&2 (saturated Ca(OH)$_2$ solution) and Stage 3 (saturated-CaCO$_3$ solution). The *Kd* values for the Stages 1&2 and Stage 3 were respectively, 297,300 and 17,510 mL/g Cd and 15,065 and 6539 mL/g Co. They speculated that the presence of sulfides in the reducing grout were responsible for the strong sorption of these divalent transition elements. Sulfides, which is present in high concentrations in slag, are known to form especially strong complexes/precipitates with Cd and Pd (*5*).
Cs, Fr, K, Rb	0	0	0.5	2	3	10	Kaplan and Coates (*4*) measured Cs *Kd* values for an SRS reducing grout containing 210 lbs/yd^3 of slag. They measured the *Kd* values in leachate simulates appropriate for Stages 1&2 (saturated Ca(OH)$_2$ solution) and

							Stage 3 (saturated-$CaCO_3$ solution). The Cs *Kd* values for the Stages 1&2 and Stage 3 were 0 and 15 mL/g respectively.
Sr, Ra, Ba	0.2	0.5	5	3	2	20	Kaplan and Coates (*4*) measured Sr *Kd* values for an SRS reducing grout containing 210 lbs/yd^3 of slag. They measured the *Kd* values in leachate simulates appropriate for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution). The Sr *Kd* values for the Stages 1&2 and Stage 3 were 2.9 and 54.6 mL/g, respectively.
Tc, Re	2500	5000	2500	5000	2500	5000	$Tc^{VII}O_4^-$ gets reduced to Tc(IV), which like other tetravalent cations sorbs strongly to surfaces. “Best” values taken from Bradbury and Sarott (*3*).
I, At	0	2	2	10	1	4	Kaplan and Coates (*4*) measured I^- *Kd* values for an SRS reducing grout containing 210 lbs/yd^3 of slag. They measured the *Kd* values in leachate simulates appropriate for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution). The Pa *Kd* values for the Stages 1&2 and Stage 3 were, respectively, 6.2 and 11.0 mL/g. They also measured an I^- *Kd* value using an artificially aged (oxidized) reducing grout and saturated-$CaCO_3$ solution (Stage 3 simulant): *Kd* value was 24.3 mL/g.
Np	1000	3000	1000	3000	150	300	Kaplan and Coates (*4*) measured Np(V) *Kd* values for an SRS reducing grout containing 210 lbs/yd^3 of slag. They measured the *Kd* values in leachate simulates appropriate for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution). The Np *Kd* values for the Stages 1&2 and Stage 3 were, respectively, 3949 and 2779 mL/g. They also measured Np *Kd* values using an artificially aged (oxidized) reducing grout and saturated-$CaCO_3$ solution (Stage 3 simulant): *Kd* value was 3265 mL/g Np.
Pa	1500	5000	1500	5000	250	500	Kaplan and Coates (*4*) measured Pa(V) *Kd* values for an SRS reducing grout containing 210 lbs/yd^3 of slag. They measured the *Kd* values in leachate simulates appropriate for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution). The Pa *Kd* values for the Stages 1&2 and Stage 3 were, respectively, 9890 and 8049 mL/g. They also measured Pa *Kd* values using an artificially aged (oxidized) reducing grout and saturated-$CaCO_3$ solution (Stage 3 simulant): *Kd* value was 24,618 mL/g Pa.
Hg	700	1000	700	1000	100	300	Kaplan and Coates (*4*) measured Hg(II) *Kd* values for an SRS reducing grout containing 210 lbs/yd^3 of slag. They measured the *Kd* values in leachate simulates appropriate for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution). The Hg *Kd* values for the Stages 1&2 and Stage 3 were 1173 and 1095 mL/g respectively. The

							relatively high Hg *Kd* values were attributed to the presence of sulfides in the reducing grout.
Sn	2500	5000	2500	5000	1000	2000	Kaplan and Coates (*4*) measured Sn *Kd* values for an SRS reducing grout containing 210 lbs/yd^3 of slag. They measured the *Kd* values in leachate simulates appropriate for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution). The Sn *Kd* values for the Stages 1&2 and Stage 3 were 71,760 and 5520 mL/g, respectively.
U	500	2500	500	2500	500	2500	UO_2^{2+} gets reduced to U^{4+}, which like other tetravalent cations sorbs strongly to surfaces. Kaplan and Coates (*4*) measured U *Kd* values for an SRS reducing grout containing 210 lbs/yd^3 of slag. They measured the *Kd* values in leachate simulates appropriate for Stages 1&2 (saturated $Ca(OH)_2$ solution) and Stage 3 (saturated-$CaCO_3$ solution). The U *Kd* values for the Stages 1&2 and Stage 3 were 2489 and 3182 mL/g respectively.

[a] References: (*1*) = Wieland and Van Loon 2003; (*2*) = Krupka and Serne 1998; (*3*) = Bradbury and Sarott 1995; (*4*) = Kaplan and Coates 2007; (*5*) = Brookins 1987.

7.0 APPENDIX B: SUPPORTING DATA, INCLUDING STANDARDS, CALIBRATION, AND BLANKS

Table 12. Efficiency calculations for the gamma spectroscopy analyses.

Calcite-saturated solution

date			9/7		9/7		9/7			
count time			6141		4663		9603		average	average
Radionuclide	Energy (keV)	Half-Life (d)	1-initial	gamma/s	2-initial	gamma/s	3-initial	gamma/s	gamma/s	efficiency
Am-241	58.6	157861.05	18130	2.95229	12641	2.71092	28593	2.97751	2.88024	0.06952
Cd-109	87.4	462.60	8107	1.32014	7568	1.62299	13451	1.40071	1.44795	0.03018
Co-57	121.6	271.79	9791	1.59437	6859	1.47094	15134	1.57597	1.54709	0.06593
Ce-139	165.5	137.60	9331	1.51946	6241	1.33841	14478	1.50765	1.45517	0.05187
Hg-203	279.3	46.61	2024	0.32959	1833	0.39309	2727	0.28397	0.33555	0.01127
Sn-113	392.2	115.10	2723	0.44341	3290	0.70555	4864	0.50651	0.55183	0.01499
Sr-85	514.4	64.84	2748	0.44748	2109	0.45228	4385	0.45663	0.45213	0.00864
Cs-137	662.9	10983.07	1416	0.23058	1086	0.2329	2223	0.23149	0.23166	0.00654
Y-88	899.5	106.60	6275	1.02182	4110	0.88141	9641	1.00396	0.96906	0.01138
Co-60	1174.2	1925.38	3876	0.63117	2545	0.54579	5839	0.60804	0.595	0.00927
Co-60	1332.7	1925.38	3280	0.53411	2275	0.48788	4882	0.50838	0.51013	0.00793
Y-88	1833.6	106.60	3530	0.57482	2435	0.5222	5515	0.5743	0.55711	0.00618

deoxygenated calcite blank 1, 2, 3

date			9/6		9/7		9/7			
count time			32540		5629		5040		average	average
Radionuclide	Energy (keV)	Half-Life (d)	1- initial	gamma/s	2- initial	gamma/s	3- initial	gamma/s	gamma/s	efficiency
Am-241	58.6	157861.05	11660	0.35833	2030	0.36063	1522	0.30198	0.34031	0.00821
Cd-109	87.4	462.60	69414	2.13319	9609	1.70705	7771	1.54187	1.79404	0.03739
Co-57	121.6	271.79	42719	1.31281	6782	1.20483	5326	1.05675	1.19146	0.05077
Ce-139	165.5	137.60	48026	1.47591	7906	1.40451	6395	1.26885	1.38309	0.0493
Hg-203	279.3	46.61	7384	0.22692	1475	0.26204	1163	0.23075	0.2399	0.00805
Sn-113	392.2	115.10	17314	0.53208	2682	0.47646	2321	0.46052	0.48969	0.0133
Sr-85	514.4	64.84	16095	0.49462	2742	0.48712	2448	0.48571	0.48915	0.00935
Cs-137	662.9	10983.07	8286	0.25464	1607	0.28549	1288	0.25556	0.26523	0.00748
Y-88	899.5	106.60	30098	0.92495	4810	0.8545	3982	0.79008	0.85651	0.01006
Co-60	1174.2	1925.38	17907	0.55031	2920	0.51874	2242	0.44484	0.50463	0.00786
Co-60	1332.7	1925.38	15783	0.48503	2607	0.46314	2018	0.4004	0.44952	0.00699
Y-88	1833.6	106.60	16857	0.51804	2858	0.50773	2331	0.4625	0.49609	0.0055

caoh2 blank 1, 2, 3

date			9/13		9/13		9/13			
count time			5324		10435		5447		average	average
Radionuclide	Energy (keV)	Half-Life (d)	1-initial	gamma/s	2-initial	gamma/s	3-initial	gamma/s	gamma/s	efficiency
Am-241	58.6	157861.05	25530	4.79527	0	0	7428	1.36369	3.07948	0.07434
Cd-109	87.4	462.60	29214	5.48723	0	0	7345	1.34845	3.41784	0.07188
Co-57	121.6	271.79	13641	2.56217	0	0	3999	0.73417	1.64817	0.07132
Ce-139	165.5	137.60	13125	2.46525	0	0	4005	0.73527	1.60026	0.05879
Hg-203	279.3	46.61	3081	0.5787	0	0	1192	0.21884	0.39877	0.01464
Sn-113	392.2	115.10	7532	1.41473	0	0	1375	0.25243	0.83358	0.02348
Sr-85	514.4	64.84	4610	0.86589	0	0	2426	0.44538	0.65564	0.01336
Cs-137	662.9	10983.07	2228	0.41848	0	0	1370	0.25151	0.335	0.00945
Y-88	899.5	106.60	8264	1.55222	0	0	2728	0.50083	1.02652	0.01253
Co-60	1174.2	1925.38	5294	0.99437	0	0	1706	0.3132	0.65378	0.0102
Co-60	1332.7	1925.38	4607	0.86533	0	0	1520	0.27905	0.57219	0.00891
Y-88	1833.6	106.60	4954	0.9305	0	0	1604	0.29447	0.61249	0.00706

deoxygenated caoh2 blank 1, 2, 3

date			9/13		9/13		9/13			
count time			5593		10075		5666		average	average
Radionuclide	Energy (keV)	Half-Life (d)	1- initial	gamma/s	2- initial	gamma/s	3- initial	gamma/s	gamma/s	efficiency
			0							
Am-241	58.6	157861.05	1269	0.22689	1612	0.16	1032	0.18214	0.18968	0.00458
Cd-109	87.4	462.60	5980	1.06919	8572	0.85082	5295	0.93452	0.95151	0.02001
Co-57	121.6	271.79	4518	0.8078	5996	0.59514	3305	0.5833	0.66208	0.02865
Ce-139	165.5	137.60	5064	0.90542	6982	0.693	4042	0.71338	0.7706	0.02831
Hg-203	279.3	46.61	1083	0.19363	2088	0.20725	1121	0.19785	0.19958	0.00733
Sn-113	392.2	115.10	3465	0.61952	4966	0.4929	3613	0.63766	0.58336	0.01643
Sr-85	514.4	64.84	2590	0.46308	4747	0.47117	2612	0.461	0.46508	0.00948
Cs-137	662.9	10983.07	1454	0.25997	2820	0.2799	1447	0.25538	0.26508	0.00748
Y-88	899.5	106.60	3415	0.61058	4591	0.45568	2586	0.45641	0.50756	0.0062
Co-60	1174.2	1925.38	2078	0.37154	2929	0.29072	1600	0.28239	0.31488	0.00491
Co-60	1332.7	1925.38	1866	0.33363	2657	0.26372	1529	0.26986	0.28907	0.0045
Y-88	1833.6	106.60	1832	0.32755	2726	0.27057	1462	0.25803	0.28538	0.00329

Table 13. Gamma analyses data from the desorption study.

Desorption Study
BM-Calcite

date	Initial	10.5												
total count	Count													
time	Rate	37251	11545	21584	44938	76519	119235	156223	193377	222847	255328	276465	299929	342646
Radionuclide	gamma/s	Initial	Interval 1	Interval 2	interval 3	Interval 4	Interval 5	Interval 6	Interval 7	Interval 8	Interval 9	Interval 10	Interval 11	Interval 12
Am-241	2.4919	92827	27836	52898	108990	184108	286329	375287	463869	534780	613006	663795	721332	823517
Cd-109	3.2125	119667	36871	69100	143796	243772	378557	496277	613799	706802	808400	874919	948620	1082315
Co-57	1.5010	55912	17157	32200	66830	113194	175780	230074	283879	326389	373700	404382	438599	499903
Ce-139	1.4158	52739	16765	30837	63628	107535	166772	218100	269485	310343	355035	384049	416158	474717
Hg-203	0.3112	11593	3399	6150	12399	20076	30143	38234	45913	51474	57713	61575	65993	73481
Sn-113	1.0842	40386	12416	23202	48346	81416	125528	163290	201223	230709	262960	284070	306815	349019
Sr-85	0.3690	13745	3839	6724	12443	18944	26523	32297	37987	41794	46055	48515	51408	56351
Cs-137	0.1937	7215	2094	3802	7693	12526	18644	23663	28864	32893	36773	39278	42103	47198
Y-88	1.0541	39267	12082	22517	46474	78233	121568	158639	195881	225252	257243	278350	301575	343159
Co-60	0.7608	28340	8809	16855	34466	57984	90049	118204	146177	168008	192643	208724	226334	258263
Co-60	0.7007	26102	7977	14946	31122	52524	81696	106751	132052	152278	174209	188349	204274	233174
Y-88	0.6168	22977	6823	12913	27094	46257	71922	93937	116123	133687	152589	164920	178712	203437
Interval count time		37251	11545	10039	23354	31581	42716	36988	37154	29470	178809	21137	23464	42717
Half interval			5772.5	16564.5	33261	60728.5	97877	137729	174800	208112	165923.5	265896.5	288197	321287.5

Rg-Deocalcite

date		10.5												
total count time		37335	11996	21895	44920	76330	119088	155949	192866	222416	254614	275763	299163	341751
Rad		Initial	Interval 1	Interval 2	interval 3	Interval 4	Interval 5	Interval 6	Interval 7	Interval 8	Interval 9	Interval 10	Interval 11	Interval 12
Am-241	0.1416	5285	2286	3827	7915	13299	20810	27426	33499	38339	43179	47015	50981	58154
Cd-109	1.1665	43553	15157	28137	57777	98129	153245	200887	248060	286361	328295	355432	385306	439687
Co-57	0.9618	35908	12927	23406	47321	80761	124875	162791	201082	232159	265539	287274	311717	355696
Ce-139	1.1351	42379	14434	26454	54517	92199	142515	186130	228957	263818	300940	325398	353497	403831
Hg-203	0.5649	21091	7163	13359	27460	46376	71463	93199	115147	132325	151346	163963	177412	201876
Sn-113	0.8197	30605	10785	19736	40233	67989	104478	136516	168044	193129	220904	239203	259183	294888
Sr-85	0.4146	15479	5295	9210	17849	28070	39825	48494	56250	62053	68400	71920	76192	83220
Cs-137	0.1753	6544	2232	4272	8543	13731	20847	26518	32294	36484	40626	43415	46458	51760
Y-88	0.8873	33129	10806	19907	41433	70104	108838	141937	175182	202062	230929	249770	270439	308761
Co-60	0.6393	23867	7895	14473	30127	50829	79863	104636	129255	148805	170480	184561	200050	228107
Co-60	0.5758	21496	6965	13082	26535	44444	69171	90478	112270	129054	147753	159273	173550	199279
Y-88	0.5127	19140	6586	11964	24505	41068	63548	82903	102433	117707	134642	145636	157957	179863
Interval count time		37335	11996	9899	23025	31410	42758	36861	36917	29550	178284	21149	23400	42588
Half interval			5998	16945.5	33407.5	60625	97709	137518.5	174408	207641	165472	265188.5	287463	320457

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