Sorption (K_d) Measurements in Support of Dose Assessments for Zion Nuclear Station Decommissioning – 14228

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ABSTRACT

The Zion Nuclear Power Station is being decommissioned. Zion*Solutions* proposes to leave much of the below grade structures in place and to fill them with "clean" concrete demolition debris from the above grade parts of the facility. The Brookhaven National Laboratory (BNL) conducted a study commissioned by Zion*Solutions* to provide site-specific data for performance assessment calculations to support the request to terminate the NRC license and allow unrestricted use of the facility. Specifically, the distribution coefficient (K_d) for five radionuclides of concern using site-specific soils and groundwater was measured by following ASTM C1733-10, Standard Test Methods for Distribution Coefficients of Inorganic Species by the Batch Method. The radionuclides of concern are Fe-55, Co-60, Ni-63, Sr-90, and Cs-137. In the testing, Sr-85 was used as an analogue for Sr-90 because it behaves similarly with respect to sorption and has a gamma emission that is easier to detect than the beta emission from Sr-90. Site-specific soils included disturbed sand (sand removed during construction and used as backfill), native sand, silt/clay and silt. In addition, two concrete cores from the Unit-1 Containment Building and the Crib House were broken into particles less than 2 mm in size and tested to obtain distribution coefficients for the five nuclides. For Fe-55 and Co-60, the soils and the concretes removed almost all of these radionuclides in solution. For Ni-63, K_d values in the soils ranged from 62 to 331 with the disturbed sand having the highest sorption for Ni. The results indicate values of K_d much greater than 1000 for Ni-63 exposed to concrete. Strontium-85 exhibited very little sorption in all media with K_d values ranging from 2 to 6 in the soils and 10 to 20 in the concretes. Cesium-137 exhibited substantial sorption in the soils with K_d values ranging from 500 to 3000 in the soils. The high K_d value for Cs occurred in the silty/clay soil. Clay is known to have a high affinity for Cs. The sorption for Cs was far lower in the concrete with K_d values ranging from 45 to 85.

INTRODUCTION

The US Nuclear Regulatory Commission identifies acceptable methods for licensees to demonstrate compliance with the radiological criteria in 10CFR20 Subpart E, the applicable regulation for termination of the Zion Station license following decommissioning. Zion*Solutions* proposes to use the method which involves a detailed radiological characterization of the final site condition. This is accompanied by a dose assessment, or performance assessment, to demonstrate that the dose criterion in 10CFR20 Subpart E is satisfied. Performance assessment (PA) models are typically run to help predict; 1) how contaminants potentially released from the reactor would move in the environment, 2) whether there are potential pathways leading to human exposure, and 3) potential impacts on human health. In order to fine-tune performance assessment models used to predict the fate and transport of contaminants in the subsurface, distribution coefficients (K_d) that reflect the behavior of specific contaminants in contact with site-specific soil and groundwater are used.

Zion*Solutions* proposes to leave much of the below grade structures in place. One of the primary options under consideration for filling the below grade structures is to use "clean" concrete demolition debris from the above grade parts of the facility. Concrete demolition debris to be placed in the basements

will be surveyed and screened to eliminate concrete that contains "detectable" concentrations of plant derived radionuclides.

The Brookhaven National Laboratory (BNL) Environmental Research and Technology Division conducted a study commissioned by Zion*Solutions* to provide site-specific data for performance assessment calculations to support the request to terminate the NRC license and allow unrestricted use of the facility. Isotope sorption testing was performed to determine distribution coefficients (K_d) for five radionuclides (both fission and activation products) resulting from operation of the Zion Nuclear Station. The isotopes of interest include Fe-55, Co-60, Ni-63, Sr-90, and Cs-137. Sorption characteristics are a function of the element, not the specific isotope, so Sr-85 which can be easily detected using a gamma counter was used as a surrogate for Sr-90. Four distinct soil samples and two distinct concrete samples along with site-specific ground water were collected at the plant site and were shipped to BNL for the study.

Based on the data generated in this sorption testing, a dose assessment calculation is expected to be performed in the next phase of study.

METHODOLOGY

Test Method

Sorption testing was performed in accordance with ASTM C1733-10, Standard Test Method for Distribution Coefficients of Inorganic Species by the Batch Method (ASTM, 2010).

This method is for the laboratory determination of the distribution coefficient (K_d), which must be used for estimating the retardation of contaminants for given site-specific geochemical conditions. It covers the determination of distribution coefficients of chemical species to quantify uptake onto solid materials by a batch sorption technique.

Test Materials

Four soil samples, two concrete samples and groundwater from the Zion site were received at the BNL.

The sample identification for soil samples and concrete samples are given in Table I.

TABLE I. Sample identification for soil samples and concrete samples.

Sample ID	Sample description	Depth	Collection date and time
CJGSSB001B	Disturbed sand	12'-15'	08/30/12 10:54
CJGSSB001C	Native sand	24'-28'	08/30/12 11:57
CJGSSB001D	Silt	31'-36'	08/20/12 13:45
CJGSSB002C	Silt/Clay	24'-28'	08/21/12 18:22
B1-01107-CJFCCV-001	U-1 Containment Building	N/A	07/26/12 07:11
B2-08101-BJFCCV-A016	Crib House Lower Floor	N/A	05/23/12 07:02

The groundwater (collection date and time, 08/30/12 10:54) was shipped in a plastic cooler to the BNL. Upon receipt, groundwater was transferred to a refrigerator and kept at approximately 4°C. The color of the groundwater was pale brown. The pH of the groundwater as received was 7.04 at 22°C.

Pretreatment of Samples

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Soil samples were used as received without any pretreatment. Concrete samples were put into a plastic bag and crushed by using a hammer. After crushing, the crushed particles were passed through a 2-mm screen and the fraction less than 2 mm was collected and used in the sorption study. The mass fraction based on particle size is provided in Table II.

The moisture content of the soil samples and the concrete samples was obtained on sub-samples by drying using a Satorius Model MA 30 Moisture Analyzer. The moisture contents of the soils ranged from 10.7-12.6% on a wet weight basis. The moisture content of the concrete samples was 4.6% (B2-08101-BJFCCV-A016) and 5.4% (B1-01107-CJFCCV-001). The moisture contents are given in Table III.

Groundwater was filtered by using 0.45 micrometer syringe filter prior to addition to the soils and the concrete samples. The pH of the groundwater was only very slightly changed after filtration.

TABLE II. Mass of each fraction of concrete samples after crushing.

Sample ID	Mass as received (g)	> 2mm fraction (g)	< 2 mm fraction (g)	Losses during crushing (g)
B1-01107-CJFCCV-001	559.0	223.6	309.6	25.8
B2-08101-BJFCCV-A016	799.0	322.6	436.4	29.3

TABLE III. Moisture content of soils samples and concrete samples.

Sample ID	Moisture content % (wet basis)
CJGSSB001B	12.6
CJGSSB001C	16.9
CJGSSB001D	15.5
CJGSSB002C	10.7
B1-01107-CJFCCV-001	5.4
B2-08101-BJFCCV-A016	4.6

Preparation of Isotope Stock Solution

The objective of this study was to determine distribution coefficients (K_d) for five radionuclides in the presence of four soil samples and two concrete samples with the site-specific groundwater. The isotopes of interest include Fe-55, Ni-63, Sr-85, Cs-137 and Co-60. The stock solutions of each isotope were prepared by addition of standard isotope solution to the deionized water. The radioactivity concentration of each isotope stock solution is given in Table IV.

TABLE IV. Radioactivity concentration of stock solution and test sample.

Isotope	Stock solution (µCi/mL)	Test sample (µCi/mL)
Fe-55	2.33	2.33E-3
Ni-63	2.54	2.54E-3
Sr-85	2.50	2.50E-3
Cs-137	3.16	3.16E-3
Co-60	0.40	4.00E-4

Sorption Study Procedure

For the equilibrium studies each sample for each soil or concrete was prepared by transferring 1 gram (dried basis) of soil or crushed concrete into a 60 mL high density polyethylene (HDPE) bottle. Triplicate samples were prepared for the equilibrium testing. Twenty five milliliters of the groundwater filtered using a 0.45 micrometer syringe filter were added to each bottle to yield a 25:1 liquid to solid mass ratio. Each of the test samples was then "spiked" with a quantity of 25 μL of each isotope stock solution added to the 25 mL solution, resulting in corresponding activity concentration expressed as μCi/mL in Table IV.

Similarly, triplicate samples without soil or concrete were prepared with deionized water, filtered groundwater and unfiltered groundwater, respectively. For each isotope, triplicate 25 mL samples of each solution were measured into 60 mL high density polyethylene (HDPE) bottles and a quantity of 25 μL of each isotope stock solution added to the 25 mL solution. The pH of filtered groundwaters after adding the isotope was measured by using an Oakton® pH700 pH meter.

In addition, in accordance with ASTM C1733-10, to ascertain the time required for the isotope/soil (or concrete) system to achieve constant activity concentration for each isotope, test samples of each soil or concrete were prepared by transferring 5 grams (dried basis) of soil or crushed concrete into 125 mL high density polyethylene (HDPE) bottles. One hundred twenty five milliliters of the filtered groundwater was added to each bottle to yield a 25:1 liquid to solid mass ratio. Each of the test samples was then "spiked" with a quantity of 125 μL of each isotope stock solution added to the 125 mL solution.

Following the preparation of test samples, the bottles were placed in a container box. The container box was shaken at 180 rpm for 7 days at room temperature (22±2°C) using an Innova 2100 Platform shaker.

To ascertain the time required for the isotope/soil (or concrete) system to achieve constant activity concentration for each isotope, an aliquot of about 2 mL was taken three times from each 125 mL bottle. Samples were collected on a one day time interval on days 4, 5, and 6 after the start of the experiment. Each aliquot was filtered using a 0.45 micrometer syringe filter and then the filtered solution of 1 mL was pipetted and transferred into a Wheaton 10 mL vial and mixed with 10 mL Ultima Gold AB scintillation fluid.

After 7 days, an aliquot of about 2 mL taken from each 60 mL bottle was filtered through a 0.45 micrometer syringe filter. One mL of the filtered solution was transferred into a Wheaton 10 mL vial and mixed with 10 mL Ultima Gold AB scintillation fluid in preparation for counting.

The pH was measured for one of the triplicate test samples and one of triplicate filtered groundwater samples to provide an indication of the change in pH of the groundwater in contact with the soil or concrete.

Radiochemical Analysis

The activity of gamma-emitting isotopes in the filtered solution was measured on a 1 mL aliquot of the sample using a Wallac LKB 1282 COMPU gamma counter with a sodium iodide detector.

A Wallac Guardian 1414 liquid scintillation counter (LSC) was used to analyze Fe-55 and Ni-63. All samples were counted for ten minutes to improve counting statistics.

For the LSC data, background radioactivity was quantified by analyzing samples of 1 mL deionized water without any added radioactivity. The background level in counts per minute (cpm) was subtracted from the gross sample count rate to obtain the net count rate. For the gamma counter, background was subtracted from the total count rate automatically. The background corrected count rates are directly

proportional to the concentration in solution and these values were used to calculate distribution coefficient (K_d).

Distribution Coefficient (K_d) Calculation

The distribution coefficient (K_d) value for each isotope was calculated using the following equation.

$$K_d = V \text{ x } (C_s - C_f) / (M \text{ x } C_f)$$

where   V = volume of filtered groundwater used, mL,
   C_s = starting activity of isotope in filtered groundwater, counts per minute (cpm),
   C_f = final activity of isotope in filtered groundwater in contact with the soil sample or the
       concrete, counts per minute (cpm),
   M = dry mass of soil or concrete sample, g.

RESULTS

The count rate in the groundwater after spiking with a radionuclide ranged from approximately 500 cpm for Co-60 to 5000 cpm for Ni-63. However, the count rate in the samples that had a sorbing media was essentially indistinguishable from background for Fe-55 and Co-60. That is, the count rate was within one standard deviation of the error in the background measurement. An error analysis is presented later and based on this analysis, a minimum K_d will be recommended based on the counting statistics. If the background corrected count rate was greater than zero, the count rates are taken as being accurate without error and the K_d is estimated. If the count rate was zero, a value of 1 cpm was used to calculate count rates. While this may underestimate the true K_d, this should not be a major problem because the calculated K_d is greater than 1000 when the count rate is indistinguishable from background.

Solution pH

The pH of the filtered groundwater increased from a value around 7.2 to near 7.7 over the duration of the tests. This is believed to be due to CO_2 present in the air. The pH of the groundwater and the pH of the groundwater in contact with the different soils were similar at the end of the test indicating the soil did not have a major impact on pH. The silt/clay soil (CJGSSB002C) tended to lower the pH by 0.3 to 0.4 pH units as compared to the groundwater. All other soils had pH values within about 0.1 pH units. The concrete had a large impact on pH causing the solution to have a pH greater than 11.5. This could be a water quality issue if massive amounts of concrete are rubblized and placed below grade in existing building structures as planned.

Iron-55

Iron-55 emits a low energy X-ray that is detected using the LSC. The equilibrium results from the triplicate samples are presented in Table V. The table presents a description of the media, the starting and final pH of the tests, the average counts per minute of the sample with the standard deviation based on the three samples, and the average K_d and standard deviation. This format is used for all nuclides in this paper.

The results indicate values of K_d much greater than 1000 for Fe-55 in all media. The count rates for the samples with the media are all extremely low and less than 10 cpm above background. This is part of the reason for the large standard deviation in K_d shown in the table. There is a large variability in the count rate of the groundwater. Comparing the average in the groundwater to that of deionized water (2042±24) suggests that the Fe is either insoluble or so reactive that it is sorbing on the particles in solution that are

filtered out. Over fifty percent of the activity in the pure groundwater has been removed (count rate 876 versus 2024). This variability in count rate of the spiked groundwater causes larger uncertainties in the calculated K_d. This variability was not found for any other nuclide.

Figure 1 shows all of the sorption data collected for Fe-55 on all sorption media. The first three data points at approximately days 4, 5, and 6 are the data collected on the approach to equilibrium and the final four data points at approximately day 8 are the triplicate samples and their average, represented by the darker color. Note that the scale for K_d on each figure is different. This format is used for all of the K_d data presented in the following figures. Due to the poor counting statistics caused by the large amount of sorption, there is substantial variability in the predicted K_d (a change from 1 cpm to 2 cpm changes K_d from 8000 to 16000). For this reason, it is not possible to judge if equilibrium has been reached.

TABLE V. Calculated K_d values for Fe-55.

Sample	Starting pH	Final pH	Counts, cpm	K_d, mL/g
Deionized water			2021± 24	
Groundwater	7.04	7.51	876±113	
CJGSSB001B		7.45	8±1	2857±481
CJGSSB001C		7.59	4±2	5579±2306
CJGSSB002C		7.33	0±1	21850±3483
CJGSSB001D		7.63	3±1	8061±3483
B1-01107-CJFCCV-001		11.52	2±1	16546±7859
B2-08101-BJFCCV-A016		11.43	0±0	21342±2709

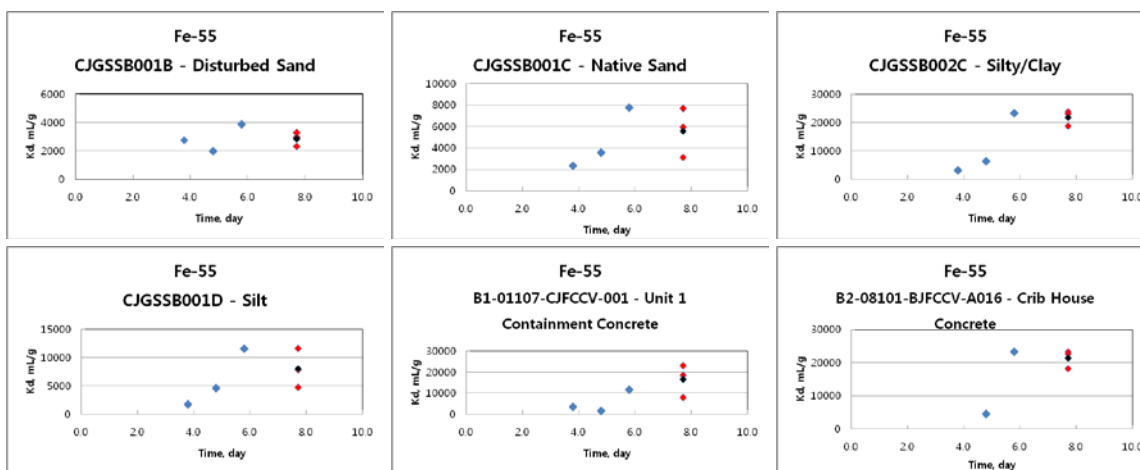- The pH was measured at the temperature of 20-24°C

Fig. 1. Measured K_d values for Fe-55 on all six media.

Nickel-63

Nickel-63 emits a low energy beta particle that was counted using LSC. The equilibrium results from the triplicate samples are presented in Table VI. In this case, the count rate of deionized water and groundwater were similar indicating that Ni-63 was soluble and not interacting with any particulate in the groundwater. In the soils (CJGSB001B, CJGSB001C, CJGSB002C and CJGSB001D), K_d values ranged

from 62 to 331 with the disturbed sand (CJGSB001B) having the highest sorption for Ni. This is somewhat surprising as the native sand (CJGSB001C) had the lowest sorption for Ni. The results indicate values of K_d much greater than 1000 for Ni-63 exposed to concrete (B1-01107-CJFCCV-001 and B2-08101-BJFCCV-A016).

Figure 2 shows all of the sorption data collected for Ni-63 on all sorption media. For the four soil media, there is a clear trend of increasing K_d for longer times. This suggests that equilibrium may not have been reached after six days. However, as the K_d increases with time the values at 8 days can be taken as a lower bound for the equilibrium K_d in the soils. The reproducibility for the triplicate soil samples was excellent with the exception of the disturbed sand which had one value much higher than the others. The two concrete samples showed reasonable agreement for the triplicate samples as evidenced by the count rate error. However, due to the low count rates, even small changes have a large impact on K_d and therefore, the error in predicted K_d is 15–25%.

TABLE VI. Calculated K_d values for Ni-63.

Sample	Starting pH	Final pH	Counts, cpm	K_d, mL/g
Deionized water			4738±75	
Groundwater	7.20	7.70	4858±58	
CJGSSB001B		7.66	360±88	331±99
CJGSSB001C		7.72	1398±24	62±2.5
CJGSSB002C		7.38	758±41	136±10
CJGSSB001D		7.74	1223±72	75±4.9
B1-01107-CJFCCV-001		11.48	37±10	3438±915
B2-08101-BJFCCV-A016		11.42	14±2	8361±1168

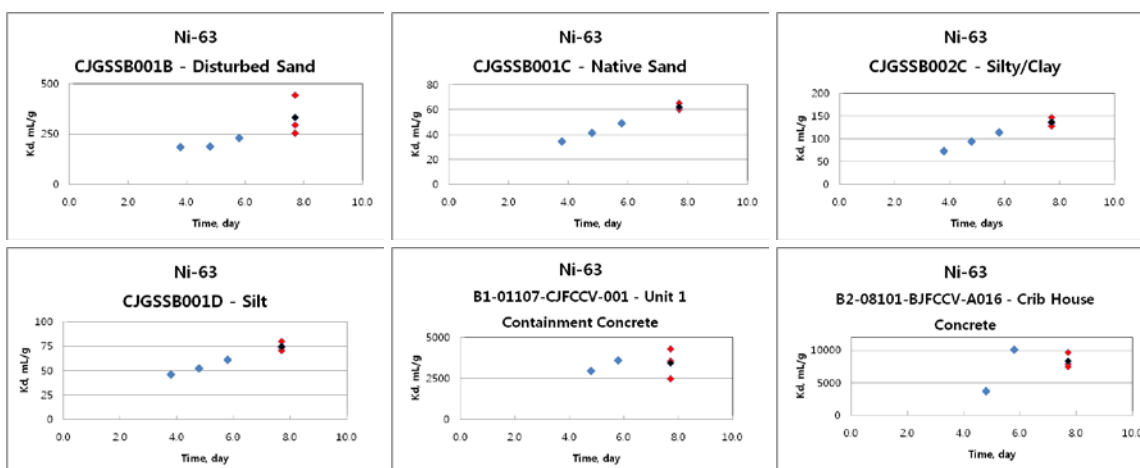- The pH was measured at the temperature of 20-24°C

Fig. 2. Measured K_d values for Ni-63 on all six media.

Strontium-85

Strontium-85 emits a 514 keV gamma ray during decay that was detected using the NaI gamma detector. The calculated K_d values for Sr after almost eight days exposure to the sorption media are presented in

Table VII. The agreement between the deionized water and groundwater count rates is excellent suggesting the water did not impact Sr availability. Strontium exhibited very little sorption in all media with K_d values ranging from 2–6 in the soils (CJGSB001B, CJGSB001C, CJGSB002C and CJGSB001D) and 10 to 20 in the concretes (B1-01107-CJFCCV-001 and B2-08101-BJFCCV-A016).

The K_d results for Sr are plotted in Figure 3 for each media. The figure suggests that Sr sorption had reached equilibrium and the results showed excellent agreement between the different samples. The results from the concrete samples are interesting. The data from days 4–6 clearly suggest equilibrium was reached. However, the final day testing showed approximately a factor of 2 lower values for K_d than in the approach to equilibrium data. There was excellent agreement between the 3 replicate samples on the final day. The cause for this discrepancy is not known. The K_d values for the concrete media from the triplicate sampling should be used as the representative K_d.

TABLE VII. Calculated K_d values for Sr-85.

Sample	Starting pH	Final pH	Counts, cpm	K_d, mL/g
Deionized water			2395±16	
Groundwater	7.20	7.80	2373±3	
CJGSSB001B		7.75	2090±21	3.4±0.3
CJGSSB001C		7.85	2172±13	2.3±0.2
CJGSSB002C		7.42	1933±11	5.7±0.2
CJGSSB001D		7.82	2175±35	2.3±0.5
B1-01107-CJFCCV-001		11.61	1675±63	10.4±1.3
B2-08101-BJFCCV-A016		11.48	1367±143	18.5±4.2

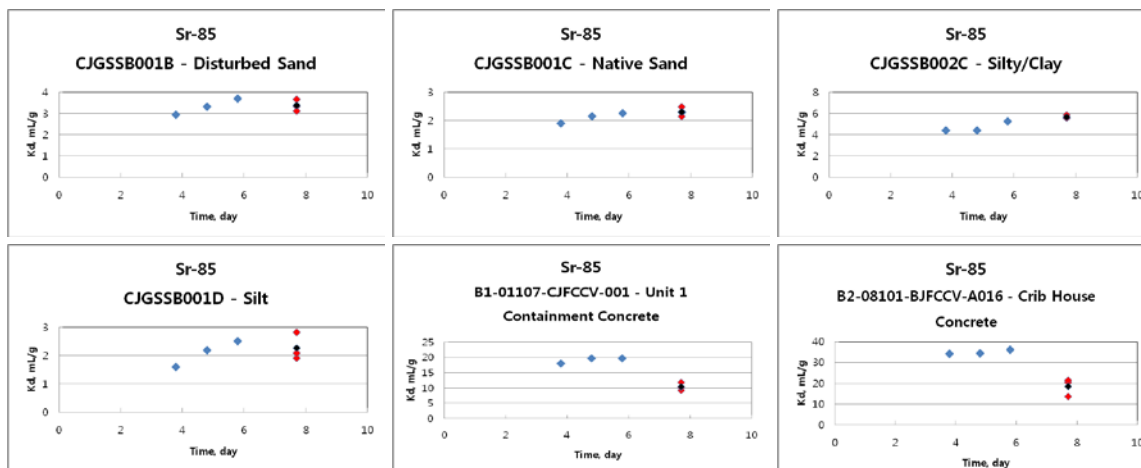- The pH was measured at the temperature of 20-24°C

Fig. 3. Measured K_d values for Sr-85 on all six media.

Cesium-137

Cs-137 was measured using the NaI gamma counter. The calculated K_d values for Cs after almost eight days exposure to the sorption media are presented in Table VIII. The agreement between the deionized water and groundwater count suggests the water did not impact Cs availability. Cesium exhibited

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substantial sorption in the soils with K_d values ranging from 500 - 3000 in the soils (CJGSB001B, CJGSB001C, CJGSB002C and CJGSB001D). The high K_d value for Cs occurred in the silty/clay soil (CJGSB002C). Clay is known to have a high affinity for Cs. The sorption for Cs was far lower in the concrete (B1-01107-CJFCCV-001 and B2-08101-BJFCCV-A016) with K_d values ranging from 45–85. This is expected for Cs.

Figure 4 shows the all K_d values obtained in these tests on the six media. The figure suggests that Cs sorption had reached equilibrium in the concrete samples and the results showed excellent agreement between the different samples. The soil samples also appeared to reach equilibrium during the tests. The K_d values of the silt sand were slightly higher than the approach to equilibrium and the values of the silt soil were slightly lower. This difference was not large and the final values presented in Table 9 should be representative of the soils.

TABLE VIII. Calculated K_d values for Cs-137.

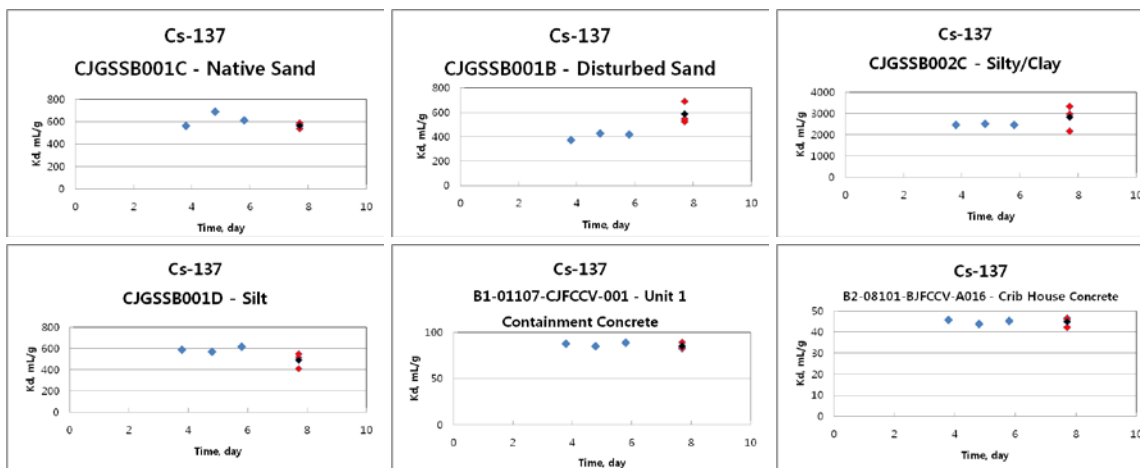| Sample	Starting pH	Final pH	Counts, cpm	K_d, mL/g
Deionized water			2952±34	
Groundwater	7.35	7.86	2960±12	
CJGSSB001B		7.72	114±18	635±96
CJGSSB001C		7.78	116±9	615±60
CJGSSB002C		7.73	24±3	3011±306
CJGSSB001D		7.83	134±5	527±17
B1-01107-CJFCCV-001		11.60	669±24	85±3.8
B2-08101-BJFCCV-A016		11.51	1052±35	45±2.4

- The pH was measured at the temperature of 20-24°C

Fig. 4. Measured K_d values for Cs-137 on all six media.

Cobalt-60

Cobalt-60 was measured using the NaI gamma detector. The stock solution count rate is similar between the deionized water and groundwater suggesting the water did not cause the removal of Co from solution. The calculated K_d values for Co after almost eight days exposure to the sorption media are presented in

Table IX. Cobalt exhibited very high sorption rates in all media with values ranging from 5000–10000 ml/g. The very low count rates after exposure to the media cause large uncertainties in the predicted K_d. For the disturbed sand (CJGSB001B), native sand (CJGSB001C), and silt (CJGSB001D), the error estimate is the same magnitude as the predicted K_d. In all other tests, the error estimate was about 50% of the predicted K_d. This will be addressed in the section on uncertainties.

Figure 5 shows the calculated K_d values for Co-60 on all six media. The extremely low count rates leads to large variations and poor reproducibility. It is not possible to judge whether equilibrium was reached in the tests. In any event, almost all of the Co is removed from solution by the contacting media in all tests.

TABLE IX. Calculated K_d values for Co-60

Sample	Starting pH	Final pH	Counts, cpm	K_d, mL/g
Deionized water			532±8	
Groundwater	7.35	7.84	522±10	
CJGSSB001B		7.67	4±3	5905±5900
CJGSSB001C		7.80	3±4	6098±5718
CJGSSB002C		7.46	2±2	9619±5615
CJGSSB001D		7.84	6±5	5293±6672
B1-01107-CJFCCV-001		11.64	1±1	8551±4209
B2-08101-BJFCCV-A016		11.51	2±2	7310±5020

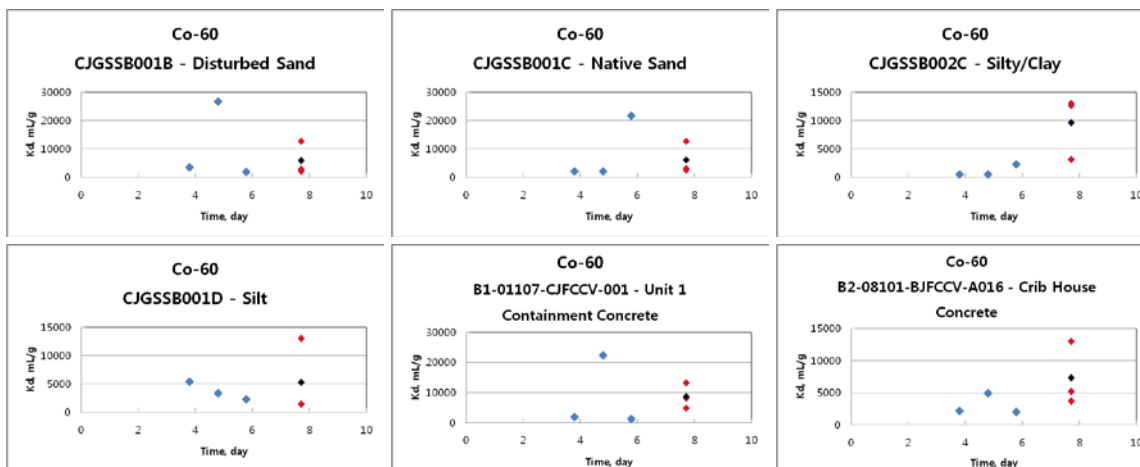- The pH was measured at the temperature of 20-24°C

Fig. 5. Measured K_d values for Co-60 on all six media.

Maximum K_d in Cases of Low Count Rates

Sources of error include measurement error on the volumes and masses, counting error, and systematic errors (for example, a scale out of calibration). The volume and mass measurement errors are less than 1% and the counting errors dominate the total error. Systematic errors are addressed through using calibrated measuring devices. A detailed error analysis was performed on the data assuming that counting error was the dominant error in the measurement system. Counting error was reduced by using sufficient

tracer to guarantee 500–5000 cpm in the stock solution. For values of K_d less than 1000 the counting error led to only a few percent error in the K_d estimate. A second type of error occurs from the natural variability in the soil samples. Although attempts were made to select representative samples, this is not possible to do precisely. This was addressed through replicate samples. For cases when the predicted K_d was less than 1000 the error due to natural variability always exceeded the counting error. In cases when K_d was greater than 1000 the count rate was so close to background that it was not clear whether natural variability or the count rate was the dominant cause in the error. In these cases, the standard deviation between the triplicate samples was often the same order of magnitude as the K_d estimate.

Iron-55 and Co-60 showed almost complete removal by the contacting media. This causes large uncertainties in the estimates for K_d. Prior to counting each set of samples a background count was collected for ten minutes. Background was automatically subtracted by the LSC and NaI gamma detector in the reported values and in the values in this report. For count rates slightly above background the process subtracts two relatively large numbers to obtain a small number. For example, for the gamma counter, the background count rate is 150.9 cpm. If the count rate of the sample is 153 cpm, the count rate above background is 2.1 cpm. The measurement error of the background and sample for ten minute counts is approximately 4 cpm. Thus, the sample count rate is less than the measurement error.

To determine a minimum K_d it is assumed that any count rate that exceeds twice the standard deviation in the background count rate is attributable to the sample. This is approximately the error in the counts above background. With this assumption the minimum count rate becomes twice the standard deviation in background. For Fe-55 forty counts were collected in the ten minute background count. This gives a standard error of 6.2 counts, or 0.62 counts per minute. Thus, the minimum background corrected count rate is 1.24 cpm. A similar calculation was performed for all nuclides and the results are summarized in Table X. The solution count rate used is the average value from the triplicate samples. The minimum background count rate is twice the standard deviation in the background counts rate.

TABLE X. Estimated K_d based on twice the standard error in the background count rate.

Radionuclide	Total Background Count in 10 minutes	Standard Error	Minimum Count rate (cpm)	Solution Count rate (cpm)	Maximum K_d (ml/g)
Fe-55	40	6.3	1.26	876	17288
Ni-63	270	16.4	3.28	4858	37002
Sr-85	1509	38.8	7.8	2373	5368
Cs-137	1509	38.8	7.8	2960	6702
Co-60	1509	38.8	7.8	522	1161

- For Fe-55 the value for deionized water is used

If these are accepted as the maximum value of K_d that can be measured with confidence this will lower the K_d values in Table V for Fe-55 and in Table IX for Co-60. Note that all calculated values for Co-60 were above the maximum value based on the error due to counting.

DISCUSSION

One of the objectives of the ASTM standard is to run the tests long enough to reach equilibrium. In this study this was attempted through collecting samples at approximately days 4, 5, and 6 to check for equilibrium and if equilibrium was reached, collecting a final sample. For the radionuclides detected using gamma counting the results from days 4, 5, and 6 showed that equilibrium appeared to be reached

for Cs and Sr after six days. The count rate for Co was indistinguishable from background. Unfortunately, during these tests the Liquid Scintillation Counter had an electronics malfunction after the fourth day. Based on the other nuclides it was decided that equilibrium would be reached for Ni and Fe after more than seven days. Samples for Fe and Ni were stored until the equipment was fixed. All samples were re-analyzed after the repairs and the results were consistent. For Ni-63 equilibrium was not reached in the soil samples as the K_d increased throughout the test. For Ni in contact with concrete equilibrium appeared to be achieved. For Fe it appeared that equilibrium was reached, however, the count rate was low and therefore, the uncertainty in this conclusion is high.

The literature contains multiple papers with K_d measurements. For perspective the values reported in Sheppard and Thibault [2] which are a summary based on values available in the literature are presented and compared to the values found in this study.

Table XI. Mean and range of K_d (ml/g) values in soils [2]

Nuclide	Sand		Loam		Clay	
	Mean	Range	Mean	Range	Mean	Range
Co	60	0.07 - 9000	1300	100 - 9700	550	112 - 2450
Cs	280	0.2 - 10000	4600	560 - 61287	1900	37 - 31500
Fe	220	5 - 6000	800	290 - 2240	165	15 - 2171
Ni	400	60 - 1600	300		650	305 - 2467
Sr	15	.05 - 190	20	0.01 - 300	110	3.6 - 32000

The need for site-specific K_d values becomes obvious from Table XI as even within a soil type the values range is several orders of magnitude. For the Zion soils the measured K_d value for Co-60 is above 1000 ml/g which is at the high end of the range of measured values. For Cs-137, the measured K_d value was 500–700 for the sands and silt with a value of over 3000 ml/g which is consistent, but slightly higher than the mean values reported in Sheppard. For Fe-55 the K_d values at Zion are at the high end of the literature values. In the tests, iron (Fe-55) was apparently insoluble as over one-half the iron in solution precipitated out of the groundwater that was not in contact with a solid media. For Ni-63 the measured K_d values at Zion are slightly lower than the mean values in the literature, but within the expected range. The K_d value for Ni-63 of native sand, 62 ml/g is at the low end of the range, but the value of disturbed sand is near the mean value in the literature. The measured values for Sr-85 are at the low end of the range reported by Sheppard. Measurements of K_d for Sr-85 at BNL [3] provided estimates of between 2 and 8 similar to the values found at Zion.

There is considerably less information available on distribution coefficients for concrete. A detailed study was conducted to support performance assessments for low-level waste disposal in 1998 [4]. This review focused on long-term issues and did not discuss Fe-55 or Co-60 due to their short half-lives. Findings from Krupka on the Ni and Sr are:
- For Ni K_d values ranged from 500 to 3000 ml/g in three separate studies.
- For Sr K_d values are expected to be in the range of 1 to 5 ml/g based on several studies. However, one study showed a K_d value of 54. An interesting finding is that in one study, Sr adsorption showed some time dependency in that the K_d increased slightly over the 150 day test period.
- In general, Cs sorption is less than Sr sorption on cements. However, for cesium there can be a large difference between adsorption onto cement versus onto concrete. Concrete is a mixture of cement (usually about one-fourth as much on a volume basis as found in cement-only pastes), sand-, pebble-, and cobble-sized aggregate material, and water. Most radionuclides appear to favor sorption onto the fine grained cement particles and the aggregate has only a minor influence on K_d. However, Cs does not readily sorb to the cement and the aggregates determine the K_d in

concrete for Cs. Generally, sorption onto pebbles and rocks is low for Cs, but it does not have to be depending on the minerals in the aggregate.

More recent studies to support performance assessment calculations at the Savannah River site [5,6] suggested K_d values similar to those found in Krupka [4]. In these reports they differentiated between oxidizing and reducing conditions with K_d values lower for reducing conditions. McDowell-Boyer [6] suggested the following values:

- For Ni K_d values ranged from 1000 to 5000 ml/g with the lower values for reducing conditions.
- For Sr K_d values are expected to be in the range of 3 to 30 ml/g.
- For Cs K_d values are expected to be in the range of 0 to 20 ml/g.

The estimated K_d values for Ni and Sr from these tests are consistent with those found in the literature. The K_d value for Cs generated in these studies is higher than previously measured values. This could be due to the aggregate material used in the concrete. Literature values are generally for sorption on cement paste. Literature values for sorption of Fe and Co on to cement were not found. However, both were above 1000 ml/g in these tests.

CONCLUSIONS

Tests have been performed to determine the distribution coefficient for five nuclides (Fe-55, Ni-63, Sr-85, Cs-137, and Co-60) on six media (four soils and two concretes) using site-specific groundwater. The tests followed ASTM C1733-10, Standard Test Method for Distribution Coefficients of Inorganic Species by the Batch Method. This test is conducted in two phases. Initially, samples are taken daily until equilibrium is reached. At this point, three replicate samples are measured. In this study, equilibrium was evaluated by examining samples collected at approximately 4, 5, and 6 days. The final samples were collected 7.7 days after the start of the tests. Liquid Scintillation Counting was used to analyze Fe-55 and Ni-63. A sodium iodide gamma detector was used to count Sr-85 (a surrogate for Sr-90), Cs-137, and Co-60. Table XII summarizes the results from these tests. Values in italics are based on a concentration of twice the standard error in count rate and represent a minimum estimate for K_d. Other values are the average K_d for the triplicate samples and the standard deviation between samples based on measured count rates.

Table XII. Best estimates for site-specific K_d (ml/g)[1].

Sample ID	Description	K_d (ml/g)				
		Fe-55	Ni-63	Sr-85	Cs-137	Co-60
CJGSSB001B	Disturbed sand	2857±481	331±99	3.4±0.3	635±96	*> 1161*
CJGSSB001C	Native sand	5579±2306	62±2.5	2.3±0.2	615±60	*> 1161*
CJGSSB002C	Silt/Clay	*> 17288*	136±10	5.7±0.2	3011±306	*> 1161*
CJGSSB001D	Silt	8061±3483	75±4.9	2.3±0.5	527±17	*> 1161*
B1-01107-CJFCCV-001	U-1 containment concrete	16546±7859	3438±915	10.4±1.3	85±3.8	*> 1161*
B2-08101-BJFCCV-A016	Crib house lower floor concrete	*> 17288*	8361±1168	18.5±4.2	45±2.4	*> 1161*

[1]Values in *italics* with the " >" symbol are based on a concentration of twice the standard error in count rate. These are a lower bound on the value of K_d.

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