October 23, 2009

MEMORANDUM TO: Gregory Suber, Chief
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THRU: Christopher McKenney, Chief   **/RA/**
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FROM: Karen Pinkston, Systems Performance Analyst
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SUBJECT: TECHNICAL REVIEW: SALTSTONE AND CONCRETE
INTERACTIONS WITH RADIONUCLIDES: SORPTION (K_d),
DESORPTION, AND REDUCTION CAPACITY
MEASUREMENTS

On January 9, 2009, the U.S. Department of Energy, Savannah River Operations Office,

provided the subject report for review by U.S. Nuclear Regulatory Commission staff (NRC)

pursuant to Section 3116(b) of the Ronald W. Reagan National Defense Authorization Act for

Fiscal Year 2005. The subject report is available on NRC's Agencywide Documents Access

and Management System (ADAMS) at accession number ML090150234. This report was

reviewed in accordance with monitoring activities described in "U.S. Nuclear Regulatory

Commission Plan for Monitoring the U.S. Department of Energy Salt Waste Disposal at the

Savannah River Site in Accordance with the National Defense Authorization Act for Fiscal

Year 2005" (ML070730363). The staff's technical review summary is attached for your use.

Docket No: PROJ0734

Enclosure: Technical Review Summary

G. Suber   2

Commission Plan for Monitoring the U.S. Department of Energy Salt Waste Disposal at the

Savannah River Site in Accordance with the National Defense Authorization Act for Fiscal

Year 2005" (ML070730363). The staff's technical review summary is attached for your use.

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Enclosure: Technical Review Summary

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DATE	10/19 /09	10/19/09	10/23/09

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Technical Review Summary: TECHNICAL REVIEW: "SALTSTONE AND CONCRETE INTERACTIONS WITH RADIONUCLIDES: SORPTION (K$_d$), DESORPTION, AND REDUCTION CAPACITY MEASUREMENTS"

Review Completed: October 2009

Reviewer(s):   K. Pinkston, D. Pickett

Document(s):   Kaplan, D.I., Roberts, K., Coates, J., Siegfried, M., Serkiz, S., *Saltstone and Concrete Interactions with Radionuclides: Sorption (K$_d$), Desorption, and Reduction Capacity Measurements*, SRNS-STI-2008-00045, Savannah River Nuclear Solutions. October, 2008. ADAMS Accession # ML090150234

Evaluation

The paper "Saltstone and Concrete Interactions with Radionuclides: Sorption (K$_d$), Desorption, and Reduction Capacity Measurements" by Kaplan et al. describes the results of experiments performed to provide additional data and model support for the performance assessment for the Saltstone Disposal Facility (SDF). This research includes the measurement of K$_d$ values for the sorption of radionuclides on simulated saltstone and Vault 2 concrete, the adsorption and desorption rates, and the measurement of the reduction capacity of simulated saltstone. Nuclear Regulatory Commission (NRC) staff had the opportunity to discuss and observe these experiments during an onsite observation visit to the Savannah River Site (SRS) on July 31, 2008. The onsite observation report for this can be found at NRC's Agencywide Documents Access and Management System (ADAMS) Accession # ML082530057.

The simulated saltstone material was made with a non-radiologically contaminated feed solution. In most cases, a simulated waste stream from the Deliquification, Dissolution, and Adjustment (DDA) process was used to create this material because this waste stream was believed to be most representative of the waste stream that is going to be disposed of at the SDF. Different leaching solutions were used to simulate different stages of the cement aging process. A portlandite saturated solution was used to simulate the first two stages of cement aging, and a calcite saturated solution was used to simulate the third stage of cement aging. The first stage of cement aging occurs immediately after the cement hardens and is characterized by high pH (>12.5), high ionic strength, the dissolution of alkali impurities, and the formation of CSH gels. The second stage of cement occurs after all of the alkali salts have been dissolved and the pH is controlled to a value of 12.5 by portlandite. In the third stage, all of the portlandite has been dissolved, the CSH gels begin to dissolve, and the pH begins decreasing.

This research was intended to gain understanding about how the radionuclides will interact with the saltstone material and vault concrete once the radionuclides have leached out of the saltstone. These studies do not address how the radionuclides are bound in the saltstone during curing, and these studies do not provide information on how the radionuclides will be leached from saltstone.

K_d Value Measurements

The solid-water distribution ratios, or K_d values, were measured for both simulated saltstone and Vault 2 concrete using batch sorption studies for I-125, Np-237, Se-75, Pa-231, Pu-238, Tc-99, U-233, and a suite of radionuclides that can be measured with gamma spectroscopy that included Am-241, Cd-109, Ce-139, Co-60, Cs-137, Hg-230, Sn-113, Sr-89, and Y-88. Measurements were made with leaching solutions that simulated both cement early in the aging process and aged cement. Additionally, measurements were made for DDA simulated saltstone under both oxidizing and reducing conditions.

The results of these experiments are presented in Tables 2 and 3. Data were not obtained for uranium because of analytical problems associated with the measurements for uranium. Additionally, a problem with precipitation of the radionuclides occurred in the no solids control sample for the suite of gamma-emitting radionuclides. The no solids control sample contained either the portlandite or calcite saturated solution and the radionuclides without the vault concrete or simulated saltstone solids. The purpose of the no solids control sample was to determine if there was a loss of radionuclides through a mechanism other than sorption onto the cementitious material, such as precipitation or sorption onto the vial.

The K_d values measured for Se, I, and Tc were lower than those reported in the literature. The lower K_d for Se was attributed to the activity of Se being near the detection limit. The measured Tc K_d values were several orders of magnitude lower than the literature value. This indicates that the Tc in these experiments was not reduced. The measured K_d values for Np and Pu were greater than previous measurements. Updated K_d values for I, Np, and Pu were recommended based on these results. The recommended K_d for iodine was changed from 2-10 mL/g to 5-9 mL/g for cement in the first two stages of aging, and from 4 mL/g to 0 mL/g for aged cement (i.e., stage 3). The recommended K_d values for Np and Pu were increased from the previous literature value. The recommended K_d value for Tc was not changed from the previous literature value of 5,000 mL/g.

NRC staff does not believe that the data from these experiments supports the continued use of the K_d value of 5,000 mL/g for Tc. Additionally, it is not clear if other literature on the K_d of Tc supports the use of this value for reducing grout. In the report by Bradbury and Sarott (1995), which was cited as the basis for the Tc K_d value in Kaplan and Coates (2007), a K_d value of 1 m^3/kg (1,000 mL/g) is recommended in Table 4. In section 5.2.10 of Bradbury and Sarott, work done by Bayliss et al. (1991) is cited in which a Tc K_d value of 5 m^3/kg (5,000 mL/g) was measured. However, this K_d value was measured in the presence of the sodium dithionite reducing agent, which is not present in saltstone, so it is not clear if this K_d value is applicable to this system. Understanding and correctly modeling the behavior of Tc is important because it significantly affects the performance and expected dose from this disposal system. As described in more detail below, the research at SRS on the K_d for Tc is ongoing. NRC staff believes that this research will be useful in addressing this issue.

Adsorption/Desorption Experiments

The rates of adsorption and desorption were measured to determine if the steady-state assumption was valid and to compare adsorption and desorption rates. The K_d approach

commonly used in modeling environmental transport assumes that both rates are same.

The rate of adsorption of the radionuclides was measured for simulated vault 2 concrete and DDA simulant saltstone in batch experiments. As was true for the K_d experiments, the experiments with the gamma emitting suite of radionuclides had problems with precipitation of the radionuclides in the no solids controls. The rates of desorption were measured using columns packed with the Vault 2 concrete and saltstone material from the adsorption experiments. The concentrations of radionuclides in the column effluent were measured with a gamma detector.

The results of these experiments indicated that the rate of desorption was much slower than the rate of adsorption for the simulated Vault 2 concrete. However, NRC staff believes that the use of the solid samples (in which there may have been problems with precipitation) to measure the desorption rates may not have been appropriate because the measured rates of desorption may be attributable to dissolution rather than desorption. Additionally, the precipitation observed in the no solid control samples may be due to an artifact of the experimental design and may not represent a phenomenon that would occur in the actual disposal system.

The rates of sorption and desorption was also measured for Tc on DDA simulant saltstone and Vault 2 concrete in a calcite saturated solution. In these experiments, the solids and calcite solution were brought to equilibrium, and then $^{99}TcO_4^-$ was added. Samples were removed and analyzed over time. After two weeks, the liquid phase was removed and replaced with a solution that did not contain Tc-99. Samples were analyzed at different times over 26 days to measure the rate of desorption.

In these experiments, very little Tc-99 was sorbed by either the Vault 2 concrete or DDA simulant saltstone. The measured K_d values in this portion of the experiment were 13 mL/g for simulated saltstone and 28.1 mL/g for Vault 2 concrete. These values are in the same range as the K_d value of 6.5 mL/g measured in the K_d experiments described above. These results indicate that Tc(VII) was not reduced to Tc(IV) because, if reduction had occurred, the Tc would have precipitated and the apparent K_d value measured would have been much higher. These results are unexpected because the saltstone and Vault 2 concrete had large reduction capacities. It was hypothesized by the researchers that the length of the experiment was not long enough for reduction to occur.

These experiments also showed that Tc sorption occurred quickly, but the rate of desorption was much slower. The paper concludes that this fact implies that if the groundwater flows along a crack and by-passes the reduction capacity of Saltstone, the oxygenated water will not promote Tc desorption as much as is predicted based on the K_d value.

NRC staff believes that it is important to understand the behavior of Tc in saltstone because as stated above the behavior of this radionuclide can significantly affect the dose from this disposal system. NRC staff also believe that additional research is needed on the relative adsorption and desorption rates of Tc. Because the Tc was not reduced in these experiments, the rates of adsorption and desorption may not be applicable to a system in which it is reduced.

Reduction Capacity Measurements

The reduction capacity and redox conditions of saltstone over time is an important factor in the performance of the system. The environmental mobility of some radionuclides, such as Tc-99, is strongly dependent on its oxidation state. A previous long-term lysimeter study at SRS showed that the addition of blast furnace slag, which contains reductants iron(II) and sulfide, to saltstone limited the leaching of Tc-99.

In the research described in this paper, the reduction capacities were measured by a titration method for a variety of materials including: DDA simulant saltstone, Vault 2 concrete, blast furnace slag, subsurface sediments, and 50 year old SRS concrete. The measured reduction capacities of the DDA simulant saltstone and Vault 2 concrete were higher than expected based on the measured reduction capacity of the blast furnace slag. The measured reduction capacity of the blast furnace slag was 832.4 µeq/g, and the measured reduction capacity of the simulated saltstone, which only contains 23% blast furnace slag, was 821.8 µeq/g. Similarly, the reduction capacity of the vault concrete was 240 µeq/g, which was higher than expected based on the vault concrete containing 10% blast furnace slag by weight. Several hypotheses were proposed for the reduction capacity in the simulated saltstone and vault concrete being higher than expected including: the higher pH of saltstone than blast furnace slag causing more of the matrix to dissolve and more of the reducing agents to be available for reaction, the saltstone could be behaving like a semiconductor, the minerals in the fly ash could be adding additional reducing capacity, and the microporosity of saltstone could be higher than blast furnace slag, which would make a larger surface area available for reaction. These results could also be attributable to the cerium used in the titration method sorbing more strongly to the saltstone than the blast furnace slag, but this was thought to be a less likely explanation.

In addition to the reduction capacity, the redox state of the system was also investigated using a Eh probe. In this experiment, the pH and Eh were measured in the effluent from a column containing DDA simulant saltstone that had an air-sparged calcite solution passed through it. It was found that the pH value decreased with the volume of water that flowed through the system. The Eh value increased quickly to around 0 mV as the oxygenated water flowed through the column. Additional experiments showed that the Eh value decreased slightly after the flow through the column had been stopped for a period of 4-6 hours. This was attributed to the system not being at steady state. The flow rate of oxygenated water through the column was much faster than would be expected in the disposal system, and the kinetics of the reducing reactions may have been too slow to create reducing conditions in the column effluent. The ability of the saltstone in the actual system to maintain reducing conditions may be better than was seen in the column experiments.

NRC staff believes that the reduction capacity and redox state of the saltstone is an important factor in the long-term performance of the saltstone, and the research described in the subject paper is extremely useful to providing model support for the performance assessment. NRC staff noted that even though the measured reduction capacity of saltstone was high, the Eh was not poised to reducing conditions in the column experiments. NRC staff agree that this was likely attributable to the high flow rate through the columns, but it would be prudent for additional experiments to be performed to confirm that the Eh will be poised to reducing conditions in saltstone that has oxygenated water flowing through it.

NRC staff discussed the research and observed some of the experiments described in the subject report during a meeting on July 31, 2008 at SRS. This discussion is summarized in an onsite observation report (ADAMS accession # ML082530057).

The subject report was also discussed with representatives of the Department of Energy and its contractors on March 25-26, 2009 at the onsite observation conducted at the Savannah River Site (SRS). A summary of the discussion is provided in the onsite observation report (ADAMS Accession No. ML091320439). The follow-up actions as a result of the discussion were:

1. Explain what measures were taken to ensure that experiments with technetium were not affected by experimental losses, such as technetium holdup in labware, resulting in underestimates of technetium concentration.

2. Clarify the pH of the calcite solution used in these experiments (page 9 and 16 state the pH=10; page 7 states that solution pH = 8.3).

3. Clarify the selenium K_d value reported in Table 5, which is different than the value reported previously in the report.

SRS staff addressed these follow-up actions in a teleconference on August 5, 2009. The meeting summary for this teleconference and supporting documents are located in ADAMS at Accession # ML092650394. The response to action 1 was that non-sediment control samples were used as an internal control for experimental losses. Actions 2 and 3 were attributed to transcription errors. The correct pH value referred to in action 2 is 8.3, and the correct value for the selenium K_d for a Stage 3 concrete referred to in action 3 is 150 mL/g.

NRC staff found these responses to be acceptable, and these three follow-up actions were closed. However, NRC staff identified a new follow-up action based on the response to action 1:

ML092650394-001. Provide details on the amount of variability observed in the measured concentration of the non-sediment control sample (i.e. C_o in Attachment 3).

Open Issues

An open issue was identified related to the research described in the subject report during the March 25-26, 2009 onsite observation conducted at SRS (ML091320439):

Open Issue 2009-1

At the SRS Saltstone Facility, DOE should demonstrate that (1) technetium-99 in salt waste is converted to its reduced chemical form in saltstone grout during the curing of saltstone grout, and is thereby strongly retained in saltstone grout, and (2) the sorption of dissolved technetium-99 onto saltstone grout and vault concrete is consistent with K_d values for technetium-99 that were assumed in the performance assessment.

SRS staff discussed their proposed approach to close this open issue during the August 5, 2009 teleconference. Their proposed approach involves performing additional testing on the saltstone reducing capacity and the K_d value of Tc-99. NRC staff agreed that the proposed approach seemed appropriate.

Conclusion

The research described in the subject report provides valuable information to support key parameters in the performance assessment. NRC staff also believes that the additional research being performed by SRS for the oxidation state and K_d value of Tc-99 in saltstone is appropriate and will provide useful information on the behavior of this radionuclide in this system.

References

Bradbury, M.H., Sarott, F.A., *Sorption Databases for the Cementitious Near-Field of a L/ILW Repository for Performance Assessment,* ISSN 1019-0643, PSI-Bericht Number 95-06. Paul Scherrer Institut. March, 1995.

Kaplan, D.I., Coates, J.M., *Partitioning of Dissolved Radionuclides to Concrete under Scenarios Appropriate for Tank Closure Performance Assessments,* WSRC-STI-2007-00640, Washington Savannah River Company. December, 2007.