## September 1, 2009

MEMORANDUM TO: Gregory Suber, Chief

Low-Level Waste Branch Environmental Protection

and Performance Assessment Directorate

Division of Waste Management and Environmental Protection Office of Federal and State Materials

and Environmental Management Programs

THRU: Christepher McKenney, Chief /RA/ by K. Pinkston for

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FROM: David Esh, Sr. Systems Performance Analyst /RA/

Performance Assessment Branch

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and Performance Assessment Directorate

Division of Waste Management and Environmental Protection Office of Federal and State Materials

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SUBJECT: TECHNICAL REVIEW: "EVALUATION OF SULFATE ATTACK ON

SALTSTONE VAULT CONCRETE AND SALTSTONE, PART I: FINAL REPORT", "EVALUATION OF SULFATE ATTACK ON SALTSTONE VAULT CONCRETE AND SALTSTONE, PART II: TEST METHODS TO SUPPORT MOISTURE AND IONIC TRANSPORT MODELING USING

THE STADIUM® CODE"

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 (NRC) staff pursuant to Section 3116(b) of the Ronald W. Reagan National Defense Authorization Act for Fiscal Year 2005. The subject reports are available on NRC's Agencywide Documents Access and Management System (ADAMS) at accession numbers ML090150306 and ML090150312.

These reports were reviewed in accordance with monitoring activities described in "U.S. Nuclear

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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

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 SummaryEnclosure: Technical Review Summary

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Technical Review Summary: "EVALUATION OF SULFATE ATTACK ON SALTSTONE VAULT CONCRETE AND SALTSTONE, PART I: FINAL REPORT", "EVALUATION OF SULFATE ATTACK ON SALTSTONE VAULT CONCRETE AND SALTSTONE, PART II: TEST METHODS TO SUPPORT MOISTURE AND IONIC TRANSPORT MODELING USING THE STADIUM® CODE"

Review Completed: June 24, 2009

Reviewer(s): D. Esh

<u>Document(s):</u> Langton, C. A., Evaluation of Sulfate Attack on Saltstone Vault

Concrete and Saltstone, Part I: Final Report, SRNS-STI-2008-00050, Revision 0, SimCo Technologies Inc. for Savannah River National Laboratory, SRNS. August 2008, ADAMS accession no. ML090150306

Langton, C. A., Evaluation of Sulfate Attack on Saltstone Vault Concrete and Saltstone, Part II: Test Methods to Support Moisture and Ionic Transport Modeling Using the STADIUM® Code, SRNS-STI-2008-00052, Revision 0, SimCo Technologies Inc. for Savannah River National Laboratory, SRNS. August 2008, ADAMS accession no. ML090150312

## **Evaluation**

The reports provide preliminary results to assess the effects of contacting saltstone vault concretes with highly alkaline solutions containing high concentrations of dissolved sulfate. Part I provides the description of and results from numerical simulations, whereas Part II provides a description of the test methods used to develop information to support the numerical modeling. Part I provides results for two surrogate concretes that were used in the preliminary durability analysis. The modeling provided key inputs for the current performance assessment (PA) analysis including but not limited to:

- The relationship between the rate of advancement of the sulfate front and the rate of change of the concrete permeability and diffusivity.
- The relationship between the sulfate ion concentration in the corrosive leachate and the rate of the sulfate front progression, and
- An equation describing the change in hydraulic properties as a function of sulfate ion concentration in the corrosive leachate.

The STADIUM® code and data from two surrogate concretes were used in the preliminary durability analysis. Validation of the results was completed for surrogate concretes. Measurements on SRS Vault 1/4 and Disposal Unit 2 concrete samples are being performed and the analysis will be revised when they are available. Modeling of and measurements on saltstone are also being performed. In addition, sulfate exposure tests of Vaults 1/4 and Disposal Unit 2 concrete samples to three alkaline, high sulfate leachates is underway to validate the predicted results. A revised report is expected to be available September 2009.

The saltstone wasteform is cast in concrete vaults. The vaults provide a barrier to movement of deleterious groundwater species into the saltstone wasteform and a barrier to migration of radionuclides in the saltstone wasteform to the environment. The studies were performed because the saltstone wasteform contains high concentrations of sulfate. Sulfate could diffuse into the vault concrete and deteriorate its performance. The measurements, analysis, and modeling were performed to estimate the degradation of the concrete over 10,000 years. The STADIUM® code is an ionic transport model that accounts for electrical coupling, chemical activity, and transport due to water gradients and temperature. The model also includes a chemical equilibrium module.

Overall the analysis and supporting measurements represented a well-designed evaluation of the potential for sulfate attack using best available technology. Three cases are evaluated: case 1 – saltstone pore water (undiluted), case 2 – saltstone pore water diluted 10:1, and case 3 – leached saltstone pore water at 10:1 dilution. Table 3-1 of the report provides previously measured saltstone pore solutions and Table 3-2 provides the values used in the simulations. The cases selected are reasonable, although, as noted in the report, the concentration of sulfate used is approximately 20% less than experimentally measured values. Experimental validation, when completed, will ensure the simulations are realistic. The U.S. Nuclear Regulatory Commission (NRC) staff will review the results of those experiments when they are available. For exposure to high sulfate concentrations (Case 1), the ettringite front was estimated to penetrate a 20 cm vault wall in about 5000 years. For cases 2 and 3 the ettringite front was estimated to penetrate approximately 40% and 20% of the vault thickness, respectively. The report discussed a number of uncertainties, such as the effect of micro cracks and macro cracks. Macro cracks (greater than 100 µm) in concrete have been previously observed to result in saturated diffusion coefficients corresponding to those reported for free water which represents about a factor of 50 increase.

Section 7.0 of Part I of the report provides a description of how the results will be abstracted for use in the PA. NRC generally agrees with the outlined approach, although modifications may be necessary when the experimental measurements are completed.

The NRC staff observes that the following areas may need to be considered by the Department of Energy (DOE) as part of model abstraction in the PA, depending on the degree to which the performance of saltstone grout, Vault 1/4 concrete, and Disposal Unit 2 is relied upon against degradation by sulfate attack: 1) consideration of fast pathways (e.g., cracks) for sulfate penetration and associated higher localized degradation, 2) new information on bulk properties of the vaults and saltstone grout, and 3) coupling of damage to reaction/transport. Each of these items is described below in more detail. NRC recognizes that the first two items would likely be addressed in the PA revision. Other questions were communicated to DOE during the March 25-26, 2009 onsite observation meeting. Those are listed in the "Teleconferences and Meetings" section of this report and are summarized below, as needed.

This study used an idealized and simplified conceptual model with one-dimensional transport for front propagation. Vaults 1 and 4 are known to have a number of imperfections (cracks, pathways around pipes or other discrete features) that would likely provide faster diffusion rates of sulfate. The calculated penetrated (degraded) wall fraction as a function of time in the PA should account for diffusion into the vault concrete (perpendicular to what is currently evaluated) at these imperfections and other features. This approach would result in earlier penetration of

some fraction of the vault wall and formation of highly-permeable pathways consistent with the damaged state of the material.

This study included measurements of the ionic diffusivity for small-scale, laboratory-prepared samples. The staff concludes that the bulk properties of the as-built materials may be significantly different due to scale, quality, or other issues. The sulfate attack and secondary phase formation processes occur at the pore and grain scale of the material. However, as discussed in these reports, the presence of macroscopic features can significantly influence the effective properties of the materials. The sulfate attack simulations should address uncertainty in the bulk properties of the as-built materials (compared to the laboratory measurements of surrogate samples used to support the analysis). At a minimum, the abstraction for the PA should include the diffusivity of the concrete as a variable.

This study did not assign higher diffusivity to the damaged region of the concrete. As the concrete is damaged, the diffusivity of the damaged region could increase resulting in a higher rate of front propagation. This effect may not be resolvable in short duration experiments because the derivative of the rate of front propagation may not be observable on the scale of such experiments. It is recommended that additional simulations be performed where the diffusivity of the degraded region is increased appropriately, and that those simulations are compared to the current simulations for common sets of input.

DOE should include uncertainty in the PA abstraction that is developed from this study. NRC staff will evaluate the revised saltstone PA when it is available.

# Teleconferences and Meetings

The subject report was discussed with representatives of the DOE and its contractors on March 25-26, 2009 at the onsite observation conducted at the Savannah River Site. 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) Evaluate the sensitivity of grid spacing to predicted front propagation in the sulfate attack evaluation.
- 2) Explain how spatial representation in the numerical experiments of sulfate attack will be translated into a PA model, since the geometries of the real system will be much more complex (e.g., a random collection of different size blocks determined by crack distributions) than those considered in the numerical experiments.
- 3) Explain how cracks are incorporated into the sulfate attack representation in the PA model, since cracks could significantly impact the degradation assessment (page 15). Explain assumption i that the transport rate of sulfate ions through damaged concrete is not different from undamaged concrete (page 21).
- 4) Clarify the conceptual model for sulfate attack. For example, does sulfate attack proceed along a front, or is it a generalized mechanism.

- 5) Clarify the conceptual model represented by case 2 (page 6). If the concentration was diluted by diffusion, then what is the fate of diffused species? If species are diffusing through the vault wall, then why isn't the vault wall degraded.
- 6) Explain why it is appropriate to neglect minor species (page A2-14).
- 7) Justify the use of Berner's approach for these materials and solutions (page A2-15).

## Open Issues

No open issues were identified as a result of the review, however as indicated above a number of follow-up actions were identified.

#### Conclusion

The NRC staff has not identified open issues associated with the methods and data reported in this study at this time. However, DOE has several follow-up actions in response to staff questions. The staff plans to review any new information developed by DOE as part of these follow-up actions.

This study contains data that will be relied upon in future performance assessment updates in support of the 2005 DOE waste determination for the Saltstone Disposal Facility. However, until such time as a PA update is completed and reviewed by NRC staff, the staff cannot fully assess the risk significance of the information. For this reason, all monitoring activities identified under Factors 1-3 of the NRC monitoring plan remain open at this time.