

November 9, 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: Christopher McKenney, Chief **/RA/**
Performance Assessment Branch
Environmental Protection
and Performance Assessment Directorate
Division of Waste Management
and Environmental Protection
Office of Federal and State Materials
and Environmental Management Programs

FROM: Karen Pinkston, Systems Performance Analyst **/RA/**
Performance Assessment Branch
Environmental Protection
and Performance Assessment Directorate
Division of Waste Management
and Environmental Protection
Office of Federal and State Materials
and Environmental Management Programs

SUBJECT: TECHNICAL REVIEW: THERMODYNAMIC AND MASS
BALANCE ANALYSIS OF EXPANSIVE PHASE PRECIPITATION
IN SALTSTONE

On November 25, 2008, the U.S. Department of Energy, Savannah River Operations Office, provided the subject report for review by NRC staff 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 ML083400055. 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

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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

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Enclosure: Technical Review Summary

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OFC	DWMEP	DWMEP	DWMEP:BC
NAME	K.Pinkston	A. Walker-Smith	C.McKenney
DATE	11/01/09	11/04/09	11/09/09

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TECHNICAL REVIEW SUMMARY: "TECHNICAL REVIEW: THERMODYNAMIC AND MASS
BALANCE ANALYSIS OF EXPANSIVE PHASE PRECIPITATION IN SALTSTONE"

Review Completed: November 2009

Reviewer(s): K. Pinkston, D. Pickett, G. Alexander, D. Esh

Document(s): Denham, M., *Thermodynamic and Mass Balance Analysis of
Expansive Phase Precipitation in Saltstone*, WSRC-STI-2008-00236,
Savannah River National Laboratory. May, 2008. Agencywide
Documents Access and Management System (ADAMS) Accession #
ML083400055

Evaluation:

The paper "*Thermodynamic and Mass Balance Analysis of Expansive Phase Precipitation in Saltstone*" by Denham described calculations performed to assess the potential for precipitation of expansive phases in saltstone. These expansive phases have higher molar volumes than normal cement minerals. The precipitation of these phases could cause fracturing that leads to a decrease in the performance of the wasteform by increasing advective flow and diffusion through it. For fracturing to occur, the amount of expansive phase minerals precipitated must exceed the ability of the porosity to accommodate the extra mineral volume, and the pressure caused by the expansive phase must be larger than the tensile strength of the cementitious material. The fraction of pore space that must be occupied before fracturing occurs is uncertain. A report by Tixier and Mobasher (2003) states that this fraction ranged from 0.05 to 0.45 for different cements with a median of 0.3.

The net volume gain from the formation of the expansive phases depends on the specific reactions involved and on whether other solid phases are consumed in the reaction. In addition, a loss in water from the pore fluid by incorporation into expansive phases can occur. The flow of water out of the pores as expansive phases precipitate may also relieve some of the pressure caused by the expansive phases.

In the subject report, the Geochemists Workbench® software was used to evaluate the potential for expansive phases to be formed in saltstone. Cement phases, including Ca-carboaluminate, CSH, C4AH13, ettringite, hydrogarnet, hydrotalcite, monosulfate, and mullite, were added to the thermodynamic database, and phases that are not typical of cements were removed from consideration. The phases allowed to precipitate included brucite, C4AH13, CSH, ettringite, gibbsite, gypsum, hydrogarnet, hydrotalcite, kaolinite, monosulfate, and quartz. The calculations were based on thermodynamic equilibrium, and kinetics were not considered. The calculations simulated the advective flow of fluid through a solid saltstone matrix in which the cement minerals were assumed to be evenly distributed. It was assumed that each new pore volume of fluid replaced the previous one with no mixing, and the reaction of each new volume of pore fluid with the solid matrix was modeled. The mineral content of the solid matrix was tracked for each volume of pore fluid reacted.

Enclosure

The primary initial mineralogy of the saltstone assumed in these calculations was estimated based on a chemical analysis of hydrated cement (WSRC 1992). The constituents identified in this analysis were placed into phases that are typical of cement. These phases included CSH, gibbsite, hematite, hydrotalcite, gypsum, and quartz. Hematite and monosulfate were not included in the phases in saltstone that were available to react with pore fluid because they rendered the model unstable. The author did not believe that this would affect the results because the amount of hematite in the initial mineralogy for saltstone was small and not including monosulfate is a conservative assumption because the volume change from this pathway is much less than the volume change from the gibbsite pathway. Two alternative initial mineralogies were also considered. One of these scenarios was based on the pre-hydrated cement composition from WSRC (1992). The other scenario was based on compositions of the portland cement, fly ash, and slag from Harbour (2006) and the salt feed composition from Dixon et al. (2008).

Six different scenarios were analyzed that considered different amounts of minerals available for reaction, different infiltrating solutions, and different initial saltstone formulations. Scenarios 1-3 used the saltstone formulation estimated based on the chemical analysis of hydrated cement. The infiltrating solution was rainwater that had been equilibrated with vault cement. Scenario 1 assumed that 10% of the minerals were available for reaction, Scenario 2 assumed 50% of the minerals were available, and Scenario 3 assumed that 100% were available. Scenario 4 also assumed an initial saltstone formulation based on the hydrated cement and 100% of the minerals being available for reaction, but in this scenario the infiltrating water was rainwater. Scenario 5 assumed an initial saltstone formulation based on pre-hydrated cement, 100% of the minerals being available for reaction, and used rainwater that was equilibrated with vault cement as the infiltrating fluid. Scenario 6 also assumed that 100% of the minerals were available for reaction and used rainwater that was equilibrated with vault cement as the infiltrating fluid, but in this scenario, the initial saltstone formulation was based on Harbour (2006) and Dixon et al. (2008).

In the Scenario 1 calculations, the expansive phase ettringite was oversaturated in the initial pore solution. The ettringite reacts with kaolinite over the initial pore volumes. The volume of ettringite then remains approximately constant for the remainder of the simulation. Another potentially expansive phase, C4AH13, was formed from the reaction of CSH and gibbsite. The calculations for Scenarios 2 and 3 had similar results, except the volume of C4AH13 increased as the fraction of minerals available for reaction. The number of pore volumes before ettringite dissolution stopped and C4AH13 precipitation began also increased as the fraction of minerals available for reaction increased. In Scenario 4, in which the infiltrating water is rainwater that has not been equilibrated with cement, the calculations predicted the minerals dissolving and a net mineral loss occurring. In Scenarios 5 and 6, in which alternative saltstone mineralogies were evaluated, the ettringite is predicted to dissolve initially and to re-precipitate later in the simulation. C4AH13 precipitation occurred after more pore volumes than in the other scenarios and the volume of C4AH13 formed is larger. The maximum amount of porosity loss due to expansive phase precipitation was observed in Scenario 6.

Based on these results, the author concluded that the fracturing of saltstone by expansive phases is unlikely because the maximum calculated loss in porosity was only 34%. This is slightly above the median value from Tixier and Mobasher (2003) for the amount of porosity that

must be filled before fracturing occurs. The results also indicate that the amount of minerals available for reaction is an important factor in the amount of expansive phase formed, with the maximum amount being formed when 100% of the minerals are available for reaction. The amount of minerals in the saltstone matrix that would be available for reaction is not well known. The mineralogy of the saltstone matrix also affects the results. In the two scenarios where alternate mineralogy was assumed (Scenarios 5 and 6), more of the expansive phase C4AH13 was formed. The composition of the infiltrating water also affected the results. In the scenario where the water had not been equilibrated with the vault cement, dissolution of the minerals occurred instead of precipitation of expansive phases.

The author identified several areas of uncertainties in this research. The first area of uncertainty was that in this research the pore fluid composition was assumed to remain constant, but it is likely that the pore fluid composition of water infiltrating through the vault concrete would change over time as the vault concrete aged. This may be a conservative assumption because pore fluid in equilibrium with aged concrete would likely have a lower pH and calcium concentration, which would likely result in less precipitation in the saltstone. Another uncertainty identified was that this research only considered the equilibrium case and kinetics were not included. There is also uncertainty in the fraction of the porosity that must be filled before fractures happen and in the long term behavior of gels. Finally, in this research, the minerals are assumed to be homogeneously distributed within the saltstone wasteform. If they are heterogeneously distributed, some pore space might be filled to a greater extent than others.

Nuclear Regulatory Commission (NRC) staff believes that this research is a good first step in developing an understanding of the potential for expansive phases to form in saltstone. In addition to the uncertainties with this research identified by the author, NRC staff also believes that there is some uncertainty associated with the selection of minerals present in the saltstone wasteform and the minerals allowed to precipitate. NRC staff also believes that there is uncertainty associated with the effect of additives and pozzolans on the dissolution and precipitation reactions. NRC staff believes that comparisons of the modeling calculations to measured data would be useful, especially data that help to constrain key uncertainties, such as the amount of porosity that must be filled before fracturing occurs, the mineralogy of the saltstone wasteform, and the percent of minerals available for reaction.

Teleconferences and Meetings:

On June 16, 2009, NRC staff provided the following questions and topics of discussion to the Department of Energy (DOE) about the subject paper.

1. Selection of Minerals

What was the basis for choosing the solid phases included in the initial saltstone normative composition (Table 3) and the suite of minerals that were allowed to precipitate in the saltstone (Table 6)? Specifically, what was the basis for including gibbsite, quartz, and kaolinite in these sets of phases? Kaolinite was included in the allowed precipitates (Table 6) despite the report's argument (in the preceding paragraph) that clays should not be included. These phases are important to some of the report's modeled reactions that involve the precipitation or dissolution of

expansive phases. For example, a reaction on page 14 suggests that ettringite (a high-molar-volume phase) is consumed by reaction with kaolinite. What effect does the inclusion of gibbsite, quartz, and kaolinite in the solid phases have on the results obtained?

2. Comparison of Results to Measured Data

What data and observations are available to compare to and constrain the modeling calculations?

3. Additives and Pozzolans

This study does not consider the effects of organic additives or pozzolanic replacement on the dissolution and precipitation of cement-related compounds. These components of concrete and grout may have an effect on the generation of expansive phases. For example, future studies could consider the effect that sulfide from the blast furnace slag might have on the phases and reactions present in this system.

4. Constraint of Modeling Results

Geochemical modeling seems to have many unknowns (initial conditions, phase selection or suppression, fundamental thermodynamic data, kinetics) that would impact the confidence in any particular result. Experiments that are designed to collect data on initial mineralogical conditions, fundamental thermodynamic data and reaction kinetics would provide much needed model support for this study.

5. Uncertainty

This study is a deterministic analysis. A probabilistic (stochastic) analysis would provide insights into the importance and sensitivity of the model results to certain thermodynamic or physical properties.

6. Kinetics

Geochemists Workbench is based on an equilibrium reaction model. However, reaction kinetics could result in metastable products that are often associated with an increase in volume. Follow on studies might consider expansive phases produced by intermediate or metastable reaction products.

7. Integration of this Research with Other Research

The staff observes that the conclusions reached in this study area could be integrated with other ongoing or recently completed studies. Dixon (2008) recently completed a study on the physical properties of grout, which included bulk porosity measurements. Updated measurements of the bulk porosity of saltstone grout may be useful in assessing whether expansive phase precipitation is likely to result in grout degradation.

These topics were discussed with staff from the Savannah River Site (SRS) site during a teleconference on August 5, 2009. The meeting summary for this teleconference and supporting documents are located in ADAMS at Accession # ML092650394.

SRS staff addressed Comment 1 by stating that the gibbsite, quartz, and kaolinite phases were included to accommodate the high concentrations of silica and aluminum relative to calcium in saltstone. It was assumed that these phases would have fewer kinetic barriers to forming than more complex clays and zeolites. Additional Geochemist Workbench runs were performed, one in which more complex minerals were allowed to precipitate and one in which kaolinite and gibbsite were suppressed and excess aluminum was put in mullite. In both cases, no significant change in the amount of minerals precipitated was observed, so these runs did not change the conclusions of the report. NRC staff asked if these results had been published, and SRS staff stated that they had not. SRS staff addressed Comments 2-7 by stating that the research documented in this report was the initial step in trying to understand expansive phase precipitation during saltstone evolution and that additional research is ongoing. NRC staff found these answers to be reasonable, but cautioned that use of research as support for assumptions and parameters in performance assessments should be consistent with the maturity of the research.

Open Issues:

No open issues were identified as part of this review.

Conclusion:

The research described in the subject paper was a useful first step in evaluating the potential for cracking of saltstone to be caused by the precipitation of expansive phases. The additional research that is ongoing on this topic will provide useful information on the expected long-term performance of the saltstone wasteform and will constrain some of the uncertainty associated with this topic. In addition, because this research only considers fractures due to the precipitation of expansive phases, research on other possible mechanisms of fracturing could be useful.

NRC staff believes that it is important for the use of research in developing a conceptual model or parameters for a performance assessment to be consistent with the maturity of the research and for the uncertainty associated with the results to be adequately accounted for. NRC staff also believes that it is important for the research that is being done in support of the performance assessment to be well integrated.

References:

Dixon, K.L., Phifer M.A., and Harbour J.R., *Task Technical and QA Plan: Saltstone Grout and Vault Concrete Sample Preparation and Testing*, WSRC-TR-2008-00037. Washington Savannah River Company, 2008.

Harbour, J.R., Hansen, E.K., Edwards, T.B., Williams, V.J., Eibling, R.E., Best, D.R., and Missimer, D.M., *Characterization of Slag, Fly Ash, and Portland Cement for Saltstone*, WSRC-TR-2006-00067, Washington Savannah River Company, 2006.

Tixier, R. and Mobasher B., *Modeling of damage in cement-based materials subjected to external sulfate attack. II: Comparison with experiments*. Journal of Materials in Civil Engineering, 15, 314-322. 2003.

WSRC. *Radiological Performance assessment for the Z-Area Saltstone Disposal Facility*, WSRC-RP-92-1360, Westinghouse Savannah River Company. 1992.