The Cementitious Barriers Partnership (CBP) Software Toolbox Capabilities in Assessing the Degradation of Cementitious Barriers – 13487

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ABSTRACT

The Cementitious Barriers Partnership (CBP) Project is a multi-disciplinary, multi-institutional collaboration supported by the U.S. Department of Energy (US DOE) Office of Tank Waste and Nuclear Materials Management. The CBP program has developed a set of integrated tools (based on state-of-the-art models and leaching test methods) that help improve understanding and predictions of the long-term structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications. Tools selected for and developed under this program have been used to evaluate and predict the behavior of cementitious barriers used in near-surface engineered waste disposal systems for periods of performance up to 100 years and longer for operating facilities and longer than 1000 years for waste disposal. The CBP Software Toolbox has produced tangible benefits to the DOE Performance Assessment (PA) community. A review of prior DOE PAs has provided a list of potential opportunities for improving cementitious barrier performance predictions through the use of the CBP software tools. These opportunities include: 1) impact of atmospheric exposure to concrete and grout before closure, such as accelerated slag and Tc-99 oxidation, 2) prediction of changes in Kd/mobility as a function of time that result from changing pH and redox conditions, 3) concrete degradation from rebar corrosion due to carbonation, 4) early age cracking from drying and/or thermal shrinkage and 5) degradation due to sulfate attack. The CBP has already had opportunity to provide near-term, tangible support to ongoing DOE-EM PAs such as the Savannah River Saltstone Disposal Facility (SDF) by providing a sulfate attack analysis that predicts the extent and damage that sulfate ingress will have on the concrete vaults over extended time (i.e., > 1000 years). This analysis is one of the many technical opportunities in cementitious barrier performance that can be addressed by the DOE-EM sponsored CBP software tools. Modification of the existing tools can provide many opportunities to bring defense in depth in prediction of the performance of

cementitious barriers over time.

INTRODUCTION

The Cementitious Barriers Partnership (CBP) (http://cementbarriers.org/) is a multi-disciplinary, multi-institutional collaboration supported by the United States Department of Energy (US DOE) Office of Tank Waste Management. The objective of the CBP is to develop a set of tools to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers used in nuclear applications. The participating institutions are Savannah River National Laboratory, Vanderbilt University and Consortium for Risk Evaluation with Stakeholder Participation (CRESP) III, Hans van der Sloot Consultancy, Nuclear Research and Consultancy Group (NRG), U.S. National Institute of Standards and Technology (NIST), SIMCO Technologies Inc., U.S. DOE, and U.S. NRC.

CBP research and development efforts are organized around a set of reference cases [1] that provide the following functions: (i) a common set of system configurations to illustrate the methods and tools developed by the CBP, (ii) a common basis for evaluating methodology for uncertainty characterization, (iii) a common set of cases to develop a complete set of parameter and changes in parameters as a function of time and changing conditions, and (iv) a basis for experiments and model validation, and (v) a basis for improving conceptual models and reducing model uncertainties. These reference cases include the following two reference disposal units and a reference storage unit: (i) a cementitious low activity waste form in a reinforced concrete disposal vault, (ii) a concrete vault containing a steel high-level waste tank filled with grout (closed high-level waste tank), and (iii) a spent nuclear fuel basin during operation. Each case provides a different set of desired performance characteristics and interfaces between materials and with the environment. Experimental and model simulation efforts to date have focused on external sulfate attack, carbonation, and primary constituent leaching phenomena [3-6, 8, 11-12].

Based on these components, the CBP has developed a suite of software for simulating reactive transport in cementitious materials and certain degradation phenomena named the “CBP Software Toolbox” [9,10,13,14]. The primary software components are LeachXS™ / ORCHESTRA, STADIUM®, and a GoldSim interface for probabilistic analysis of selected degradation scenarios. The current version supports analysis of external sulfate attack (including damage mechanics), carbonation, and primary constituent leaching. The LeachXS™ component embodies an extensive material property measurements database with emphasis on cementitious materials used in DOE facilities, such as Saltstone (DOE Savannah River site) and Cast Stone (DOE Hanford site), tank closure grouts, and barrier concretes. The US EPA Leaching Environmental Assessment Framework (LEAF) (http://vanderbilt.edu/leaching/) test methods are also applicable to soils remediation and evaluation of alternative waste forms and treatment process effectiveness.

SALTSTONE PERFORMANCE ASSESSMENT APPLICATION

A 2009 CBP review of DOE Performance Assessments (PA) identified external sulfate attack associated with the Saltstone Disposal Facility (SDF) at the DOE Savannah River Site [7] as a timely opportunity for the CBP to provide a tangible benefit to the PA process. Saltstone is a cementitious waste form made by mixing salt solution originating from liquid waste storage tanks at the DOE Savannah River Site with a dry mix containing blast furnace slag, fly ash, and cement or lime. The wet mix is poured into a concrete repository for on-site disposal. Solidified Saltstone is a dense, alkaline, reducing, micro-porous, monolithic, cementitious matrix, containing a solution of salts within its pore structure. Sodium sulfate concentrations in the pore fluid are around 0.15 mol/L, and external sulfate attack on concrete barriers is expected to occur over time. The physical damage associated with sulfate attack is commonly associated with the formation of ettringite, an expansive mineral phase relative to its reactants. Salt waste is contained within the SDF via the low-permeability waste form (grout) and a low-permeability concrete barrier that encapsulates the waste. Inclusion of ground blast furnace slag in the grout and concrete dry mixes further creates reducing conditions that chemically impede the release of Tc-99.

The SDF was selected for the initial PA support effort because 1) cementitious waste forms and barriers play a prominent role in the performance of the facility, 2) the long-term hydraulic and chemical behaviors of cementitious materials composing the facility were uncertain considering exposure to sulfate residing in the wasteform pore water, and 3) review of the SDF PA by external stakeholders was ongoing, providing an opportunity to impact the process. The LeachXS™ / ORCHESTRA, STADIUM®, and uncertainty components of the current CBP Software Toolbox were used to re-assess the potential for sulfate attack damage, resulting in several technical insights relative to the 2009 SDF PA [2, 5, 6, 11], summarized as follows:

1. Material layers: A three-layer soil-concrete-waste model is not necessary for accurate prediction of ettringite front depth. Similar simulation results were observed for 3 meters, 1 meter, and no soil layers. A two-layer concrete-waste model is adequate for predicting external sulfate attack with STADIUM®. Additional simulations were performed using waste thicknesses of 50, 100, 200, 300 and 500 cm. STADIUM® results indicate that a waste thickness of at least three meters (300 cm) is needed in a two-layer model for long-term (10,000+ years) durability simulations [6].

2. Computational mesh resolution: The baseline simulations were performed using 50 elements in the concrete layer and 120 in the salt waste layer. Two additional simulations were performed with ±20% cell numbers. Ettringite is an expansive mineral phase associated with sulfate attack; profiles of the mineral after 10,000 years are practically identical for all three mesh schemes [6], indicating numerical dispersion is negligible at the nominal mesh

resolution. The SDF PA analysis incorporated 90 elements in the concrete layer, which implies more than adequate computational mesh resolution.

3. Sulfate concentration at interface: The initial mineral assemblage and pore solution in the salt waste form are based on laboratory/room temperature conditions, about 23ºC. The sulfate concentration in the simulated pore solution at this temperature is 131 mmol/L [6]. The long-term field exposure condition is roughly 15ºC, the assumption for STADIUM® exposure simulations. Lowering the temperature from 23ºC to 15ºC to begin long-term durability simulations produced a lower sulfate concentration in the salt waste form, approximately 77 mmol/L [6] or 40% lower than laboratory conditions. These observations indicate that the sulfate exposure levels assumed in the SDF PA, which are based on data from laboratory (room temperature) conditions, may be biased high relative to long-term field conditions. Furthermore, STADIUM® simulations indicate that the sulfate concentration at the concrete-waste interface declines significantly over time [6]. The SDF PA analysis incorporates an interface concentration that is fixed through time at the initial value. The CBP simulations indicate that the SDF PA sulfate exposure levels are overestimated in out years, and over predict ettringite front movement (all else being equal).

4. Initial mineral assemblage: An alternative initial mineral assemblage was considered as a sensitivity exercise to specifically illustrate the possibility that ettringite does not form in concrete despite sulfate exposure from the adjoining salt waste form. The CBP concluded [6] that "the most important result concerns the influence of different mineral assemblages in the Saltstone mixture. The second set of minerals used for the simulations did not initiate the penetration of an ettringite front in the concrete barrier despite the high sulfate concentration in the pore solution. The absence of ettringite means that the concrete is not subject to sulfate attack and could prove highly durable for an extensive period of time. This surprising result emphasizes the need for experimental research work in order to have a better understanding of the complex interaction between the salt waste material and the concrete barrier." This insight could potentially be used to develop alternative Saltstone and/or concrete formulations that are more resistant to external sulfate attack by design.

5. Durability (time for full penetration of sulfate attack front) is seen to be roughly inversely proportional to the sulfate exposure concentration as expected.

6. Incorporation of mineral availability into the analysis significantly reduces concrete barrier longevity. External sulfate attack progresses at a faster rate when fewer solid reactants are locally available to consume incoming solute reactants.

7. At lower mineral availability, the LeachXS™/ORCHESTRA and STADIUM® mineral sets produce comparable durability predictions. At higher (total) mineral availability, predictions

are sensitive to the initial mineral set, especially at higher sulfate exposure.

Using the insights described above, it was suggested that the external sulfate attack model described in References [3-5] could be used to generate more representative and reliable probabilistic predictions of Saltstone concrete durability through the following enhancements:

1. Create a two-layer model to more accurately simulate conditions at the Saltstone-concrete interface.

2. Define an accurate input distribution for sulfate concentration in Saltstone pore solution based on field monitoring data from ongoing SDF operations.

3. Refine and validate the initial mineral set through additional laboratory characterization of representative concrete samples.

4. Investigate whether mineral availability measurements in short-term experiments are valid for long-term durability simulations, and make corresponding modeling assumptions for mineral availability. Short-term data may underestimate the availability of certain minerals.

OTHER PERFORMANCE ASSESSMENT APPLICATIONS

Since the 2009 CBP review of DOE PAs, the influence of carbonation on the corrosion rate of steel embedded within cementitious materials has been identified by the CBP as another critical need for improved predictive capabilities. Embedded steel occurs in the common form of reinforcing bar (rebar) material, and as the primary tank liner in the context of DOE liquid radioactive waste tank closures. Damage to cementitious barriers and waste forms is considered a primary degradation phenomenon in many DOE applications. In response, development efforts to add carbonation modules to the CBP Software Toolbox began in 2012 and the initial Toolbox release includes one based on LeachXS™/ORCHESTRA. Refinement of that module (e.g. enhanced graphics and materials database) and addition of a STADIUM®-based module are anticipated in 2013.

Another important phenomenon is retention of Tc-99 in slag-bearing cementitious waste forms and barriers, the DOE Saltstone Disposal Facility being an example. Ground blast furnace slag is included in the waste grout and concrete barrier dry mixes to create reducing conditions and effectively immobilize Tc-99 as Tc(IV). Also in 2012 the CBP began development of a Toolbox module for simulating slag/Tc oxidation via oxygen transport in both the liquid and gas phases.

Recognizing that physical damage to cementitious materials typically occurs in the form of cracking, ongoing CBP development efforts are also focused on predicting damage through fracture mechanics considerations, determining the hydraulic and transport properties of fractured materials, and implementing corresponding Toolbox simulation capabilities.

CONCLUSIONS

Components of the CBP Software Toolbox have been used to provide important technical insights to the DOE PA process regarding sulfate attack on the DOE Saltstone Disposal Facility. Current development efforts in the areas of carbonation, gas and liquid phase oxidation of ground blast furnace slag and Tc-99, damage mechanics, and flow and transport in fractured cementitious materials will enable further tangible contributions to DOE PAs.

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