Cementitious Barriers Partnership (CBP): Using the CBP Software Toolbox to Simulate Sulfate Attack and Carbonation of Concrete Structures – 13481

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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 Office of Tank Waste Management. The CBP project has developed a set of integrated modeling tools and leaching test methods to help improve understanding and prediction of the long-term hydraulic and chemical performance of cementitious materials used in nuclear applications. State-of-the-art modeling tools, including LeachXS™/ORCHESTRA and STADIUM®, were selected for their demonstrated abilities to simulate reactive transport and degradation in cementitious materials. The new U.S. Environmental Protection Agency leaching test methods based on the Leaching Environmental Assessment Framework (LEAF), now adopted as part of the SW-846 RCRA methods, have been used to help make the link between modeling and experiment. Although each of the CBP tools has demonstrated utility as a standalone product, coupling the models over relevant spatial and temporal solution domains can provide more accurate predictions of cementitious materials behavior over relevant periods of performance. The LeachXS™/ORCHESTRA and STADIUM® models were first linked to the GoldSim Monte Carlo simulator to better and more easily characterize model uncertainties and as a means to coupling the models allowing linking to broader performance assessment evaluations that use CBP results for a source term.

Two important degradation scenarios were selected for initial demonstration: sulfate ingress / attack and carbonation of cementitious materials. When sufficient sulfate is present in the pore solution external to a concrete barrier, sulfate can diffuse into the concrete, react with the concrete solid phases, and cause cracking that significantly changes the transport and structural properties of the concrete. The penetration of gaseous carbon dioxide within partially saturated concrete usually initiates a series of carbonation reactions with both dissolved ions and the hydrated cement paste. The carbonation process itself does not have a negative effect, per se, on the paste physical

properties and can even result in reduced porosity and can help form a protective layer at the surface of concrete. However, carbonation has been shown to increase leaching of some constituents and can potentially have a detrimental effect on reinforced concrete structures by lowering pH to ca. 9 and depassivating embedded steel (e.g. rebar) and accelerating corrosion, which are important processes related to high-level waste tank integrity and closure evaluations. The use of the CBP Software ToolBox to simulate these important degradation phenomena for both concrete vaults and high-level waste tanks are demonstrated in this paper.

INTRODUCTION

There is broad use of cementitious materials in nuclear applications (e.g., waste disposal systems and nuclear facility components). Often cement barriers represent primary controls to prevent radionuclide and contaminant releases from nuclear facilities. Significant degradation of these barriers can provide a mechanism for contaminant release to the environment, and modeling these barriers presents difficulties to performance assessment assessors because of a lack of the consensus, mechanistic models needed to accurately predict their performance. Often these barriers are ignored or considered "conservatively" in assessments, which often limits the amount of waste that can be emplaced for disposal or left in place for closure. Improved models and supporting test methods are needed to better reflect the actual long-term effectiveness of cement materials in these applications.

The Cementitious Barriers Partnership (CBP) Project [1] is a multi-disciplinary, multi-institutional collaborative effort supported by the U.S. Department of Energy (US DOE) Office of Tank Waste Management. The goal of the CBP is to develop the next generation of simulation tools and corroborative experimental methods needed to assess the structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications over extended time frames. The CBP has developed and released a set of integrated tools, namely the CBP Software ToolBox, that improve understanding of the performance of cementitious materials used in nuclear applications [1,2].

Two important degradation phenomena were selected for initial demonstration: sulfate ingress / attack and carbonation of cementitious materials. When sufficient sulfate ions are present in the pore solution external to a concrete barrier, the ions can diffuse into the concrete pores and react with the concrete solid phases to form expansive mineral phases that can cause cracking changing the transport and structural properties of the concrete (Fig. 1). When gaseous carbon dioxide penetrates partially saturated concrete, a series of reactions with both dissolved ions and the hydrated cement paste begin (Fig. 1). The carbonation process does not have a deleterious impact, *per se*, on the physical properties of the cement and can even result in reduced porosity and a protective layer at the surface of concrete. However, carbonation can increase constituent leaching and potentially lead to depassivating embedded steel (e.g., rebar) accelerating corrosion, which are important processes related to high-level waste (HLW) tank integrity and closure evaluations. The use of the CBP Software ToolBox to simulate these important degradation phenomena for concrete vaults and HLW tanks are illustrated in this paper.

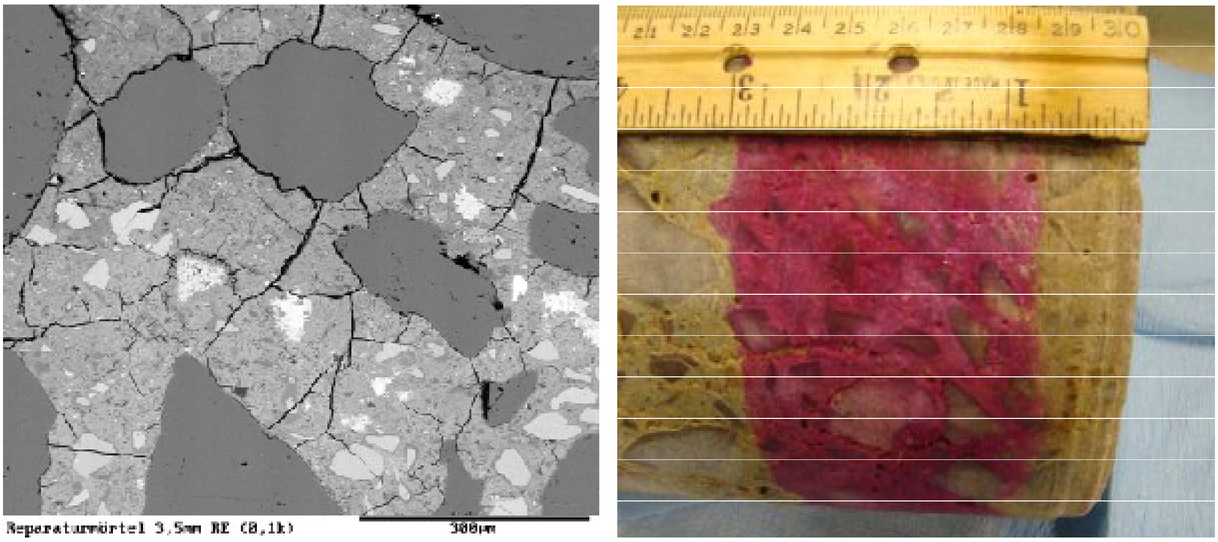

Fig. 1. Examples of Sulfate Attack (left) [3] and Carbonation (right) [4] in Concrete

SCENARIOS MODELED IN THE CBP SOFTWARE TOOLBOX

Two important cement degradation phenomena (i.e., sulfate ingress/attack and concrete carbonation) and constituent leaching can be simulated using the CBP Software ToolBox. These phenomena have the potential to impact current USDOE waste management processes, and an improved ability to characterize and predict the performance of the cement barriers and waste forms used would help provide more accurate predictions for relevant performance assessments.

For the current CBP Software ToolBox, available scenarios can be summarized as one-dimensional transport through a series of porous layers (Fig. 2), at least one of which is a cementitious material [2]. As configured for the ToolBox, STADIUM® [5] can predict sulfate ingress (and presumed damage) for either a two- or three-layer model. LeachXS™/ORCHESTRA [6] can predict sulfate attack and corresponding damage (based on continuum mechanics) for a concrete vault exposed to a leachate with a high sulfate ion concentration (representing salt waste form). LeachXS™/ORCHESTRA can also predict the carbonation front for a single-layer case representing a HLW tank integrity scenario (or carbonation and oxidation coupled with leaching of major constituents and radionuclides from waste forms). The desired simulation case (represented in Fig. 2) can be selected in the CBP Software ToolBox using the GoldSim Dashboard shown in Fig. 3.

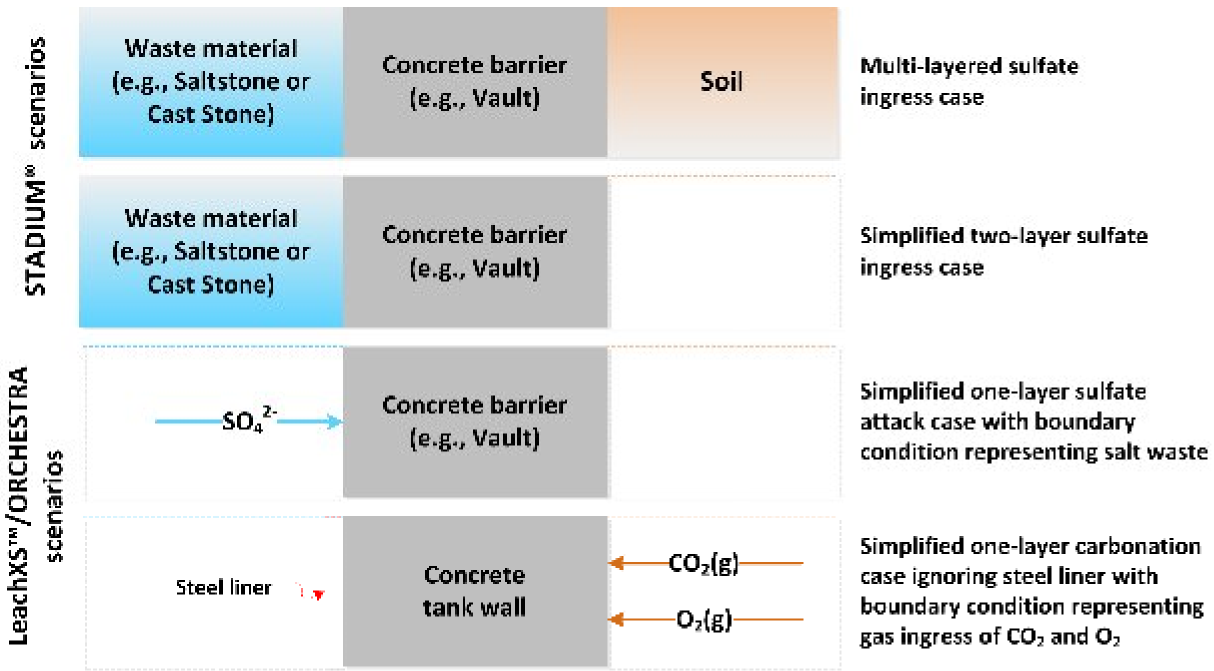

Fig. 2. Representation of CBP Software ToolBox Demonstration Cases [1]

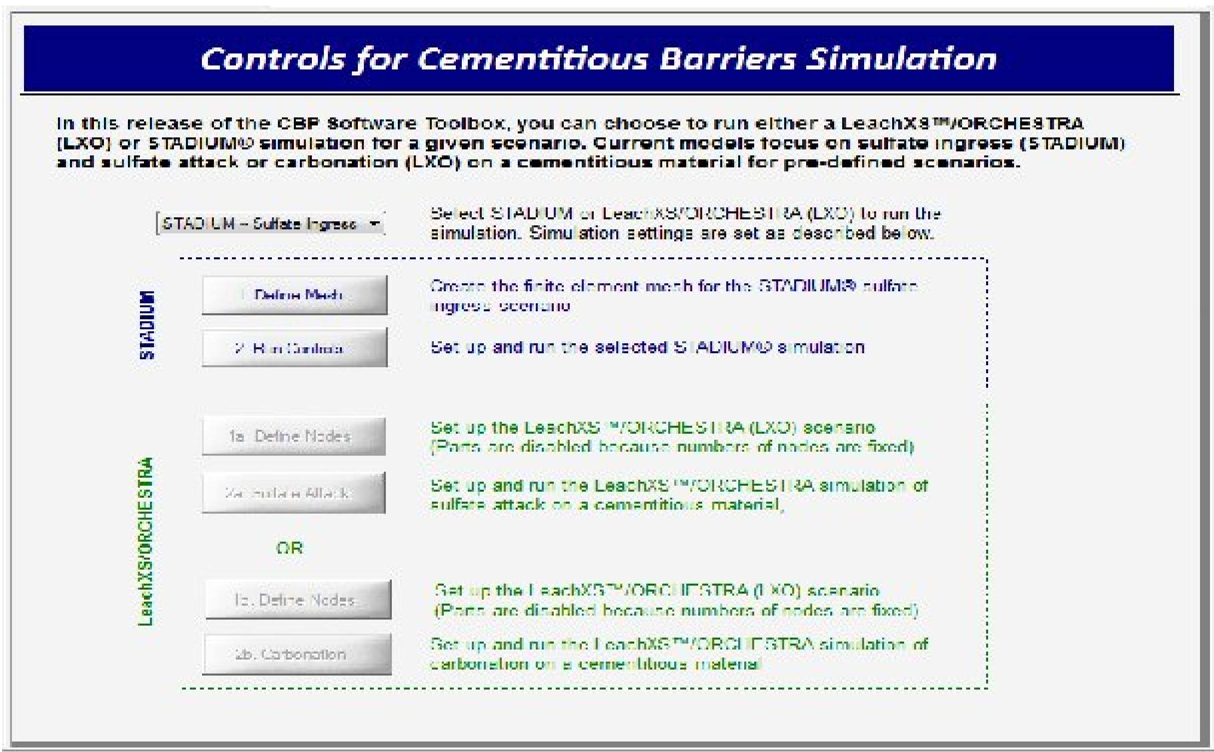

Fig. 3. Dashboard to Select CBP Software ToolBox Simulation Cases

MODELING EXTERNAL SULFATE INGRESS AND ATTACK

External sulfate attack results from the ingress of sulfate ions (e.g., leached from a salt waste) into the concrete barrier pore solution. When sulfate ions react with the cement hydration products, expansive mineral phases (e.g., gypsum and ettringite) may form that can fill pore spaces and eventually cause cracking and loss of strength. The transport properties of the resulting cracked concrete are different and can promote increased constituent release and migration.

Either STADIUM® or LeachXS™/ORCHESTRA can be called from the CBP ToolBox to model the potential impact of high sulfate waste in contact with a concrete barrier. Both models have been shown to qualitatively agree with experimental results generated by SIMCO Technologies, Inc. to validate their sulfate ingress predictions [7]. The two models have different capabilities that help complement each other.

STADIUM® is typically used for service life prediction of large, concrete structures and is concerned with bulk species. The model is based on a Sequential Non Iterative Algorithm (SNIA) that separately solves transport equations and chemical equilibrium relationships. The transport equations are discretized using the finite element (FE) method and solved simultaneously using a coupled algorithm. The calculation core begins a time step by solving the transport conservation equations without considering chemical reactions. There are four main components to the transport conservation equations: ionic transport, electrodiffusion potential, moisture transport, and temperature (energy) conservation. When this step has converged, the chemical function analyses each node of the FE mesh and makes sure that the pore solution concentrations and the mineral phases are in equilibrium. When this is completed, another time step starts.

LeachXS™/ORCHESTRA can be used to simulate ingress and leaching of bulk and trace species including radionuclides (using the full underlying geochemistry of the cement system consistent with state-of-the-art thermodynamic data) as well as transport for both experimental and field contaminant release situations. The chemical and physical model components in both models can be used as part of a larger scale release scenario supporting environmental impact assessments.

STADIUM® Modeling of External Sulfate Ingress

STADIUM®, available from SIMCO Technologies, Inc. [5], can be used for service life prediction of large, concrete structures exposed to aggressive environments (e.g., those with high chloride or sulfate concentrations) and is primarily concerned with bulk species from a mineralogical perspective [5,8]. Generally, STADIUM® models are initially developed using the model's graphical user interface (GUI). This method allows the user to easily define the desired solution geometry, material properties, input parameters, boundary conditions, etc. that are saved in a set of text files used to control the simulation. Because of the complexity of the STADIUM® input files and how they are created, it is recommended that the initial model be created using the

STADIUM® GUI.

A one-dimensional, multi-layer sulfate ingress model (Fig. 2) was developed by SIMCO Technologies, Inc. for use in the CBP Software ToolBox [9]. The STADIUM® model was incorporated into the ToolBox and can be run using the appropriate GoldSim Dashboards. A finite element mesh scheme is originally defined for the scenario using the STADIUM® GUI. The first step in using the sulfate ingress modeling using the CBP Software ToolBox is to verify that the finite element mesh scheme is appropriate because the user can change parameters (e.g., number of layers and number of nodes) that might impact the mesh. The appearance of the resulting mesh can be verified using Dashboard controls.

The next step in STADIUM® modeling using the ToolBox is to select the materials that will be modeled in the various layers (Fig. 4) as well as the thickness of the layers and the coefficients of variance (COVs) associated with the measured concentrations for the materials. The properties of the available materials are currently maintained in an Excel spreadsheet with plans for migration to an Access database in the next version of the ToolBox. The user can vary parameters controlling the STADIUM® solution methods. Finally, the user selects whether to run the model deterministically or probabilistically and the corresponding simulation parameters.

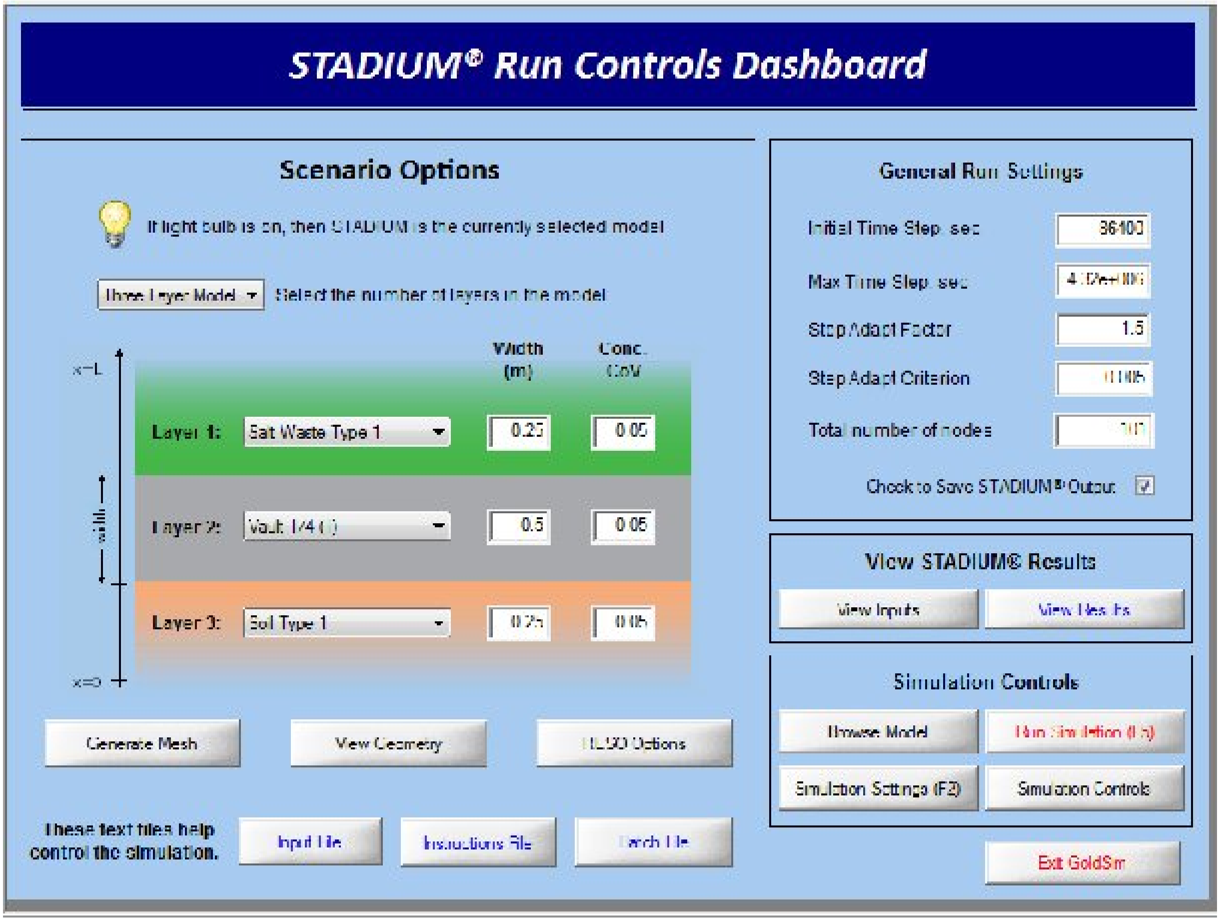

Fig. 4. Dashboard to Control the STADIUM® Simulation

When the STADIUM® model is selected from the GoldSim Dashboard, a custom STADIUM® executable is called using the CBP custom Dynamic-link Library (DLL) [10] that uses the input generated from the Dashboards to run the model. After the run completes, the results generated by STADIUM® are retrieved by GoldSim using the CBP custom DLL. Model results can be viewed using a set of pre-defined GoldSim graphs. A typical output from the STADIUM® model is shown in Fig. 5 [11]; there are plans for adding custom graphics capabilities to the next version of the ToolBox.

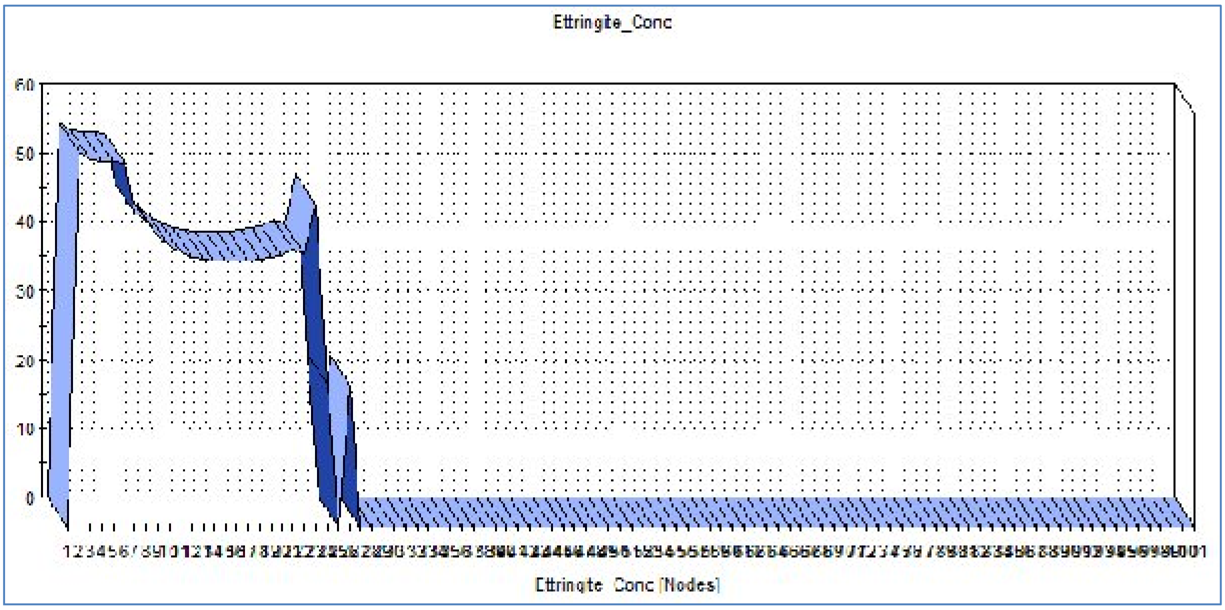

Fig. 5. Example STADIUM® Ettringite Results as a Function of Node Number [10]

LeachXS™/ORCHESTRA Modeling of External Sulfate Attack

LeachXS™/ORCHESTRA [6] embodies a database for a wide range of materials (cement barrier, grout and waste) and can be used to simulate different contaminant release situations including the state-of-the-art experimental procedures (USEPA Methods 1313 – 1316 in SW-846) used to evaluate performance under well-defined conditions. The LeachXS™ Pro application can be used (Fig. 6) to develop a custom model for a desired scenario. The ORCHESTRA code is integrated into LeachXS™ and provides geochemical speciation model and transport modeling capabilities [12].

Using LeachXS™ Pro, a sulfate attack model was developed for the CBP Software ToolBox based on the work of Sarkar [13]. The model constitutes a one-layer, one-dimensional model (Fig. 2) with a boundary condition representing sulfate in an external salt waste layer. The number of nodes and dimensions for the sulfate attack model are fixed based on previous research; thus the functionality in the corresponding GoldSim Dashboard is currently disabled. The type of concrete in the layer and various LeachXS™/ORCHESTRA simulation parameters can be set using the corresponding GoldSim Dashboard (Fig. 7). Simulation parameters (e.g., Monte Carlo) can be set using built-in GoldSim controls. Additional variants of the sulfate attack model (e.g., two- and three-layer models with non-uniform node dimensioning) have been investigated and will be included in subsequent versions.

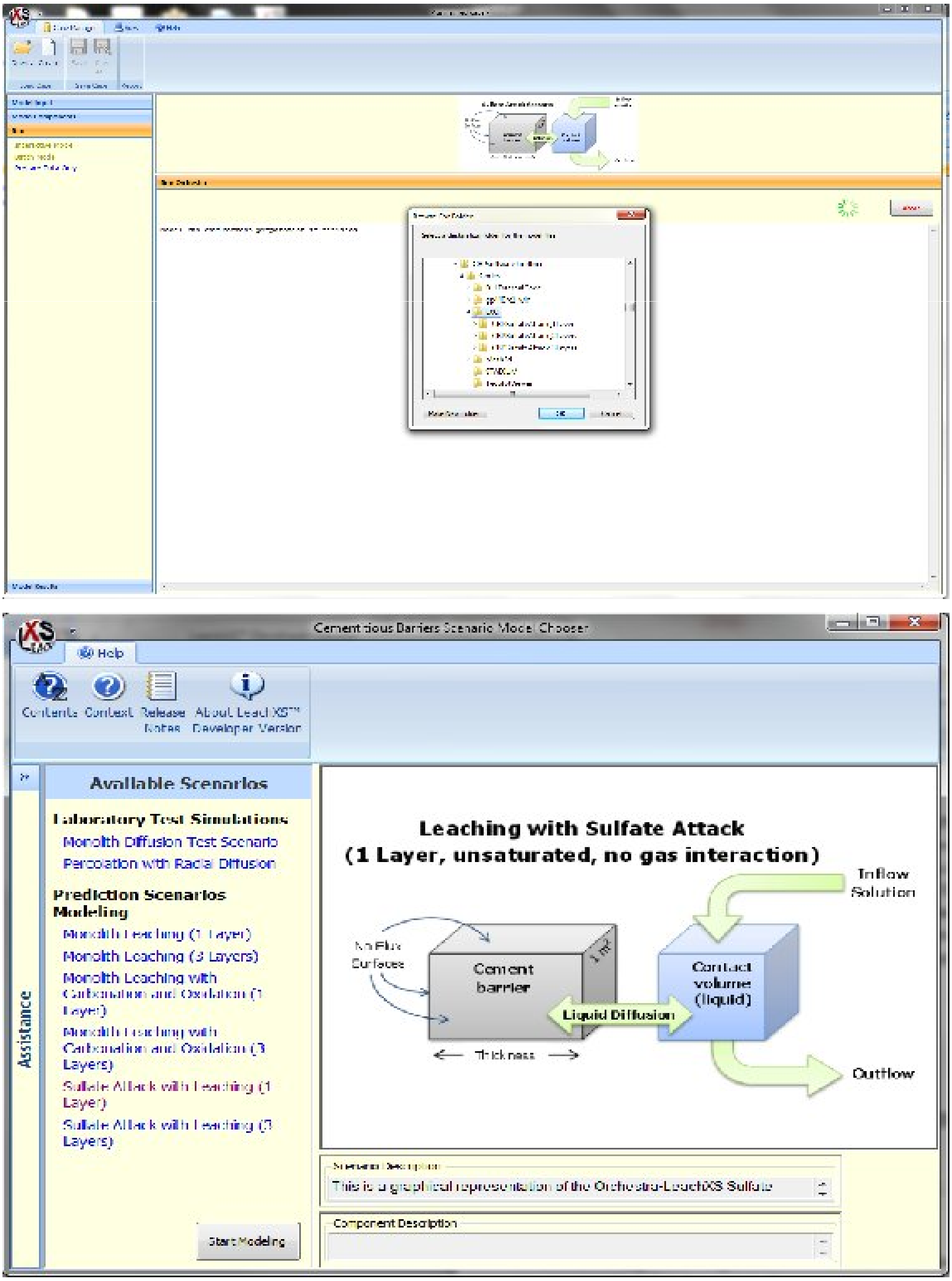

Fig. 6. Using LeachXS™ Pro to Develop a Model for the CBP Software ToolBox

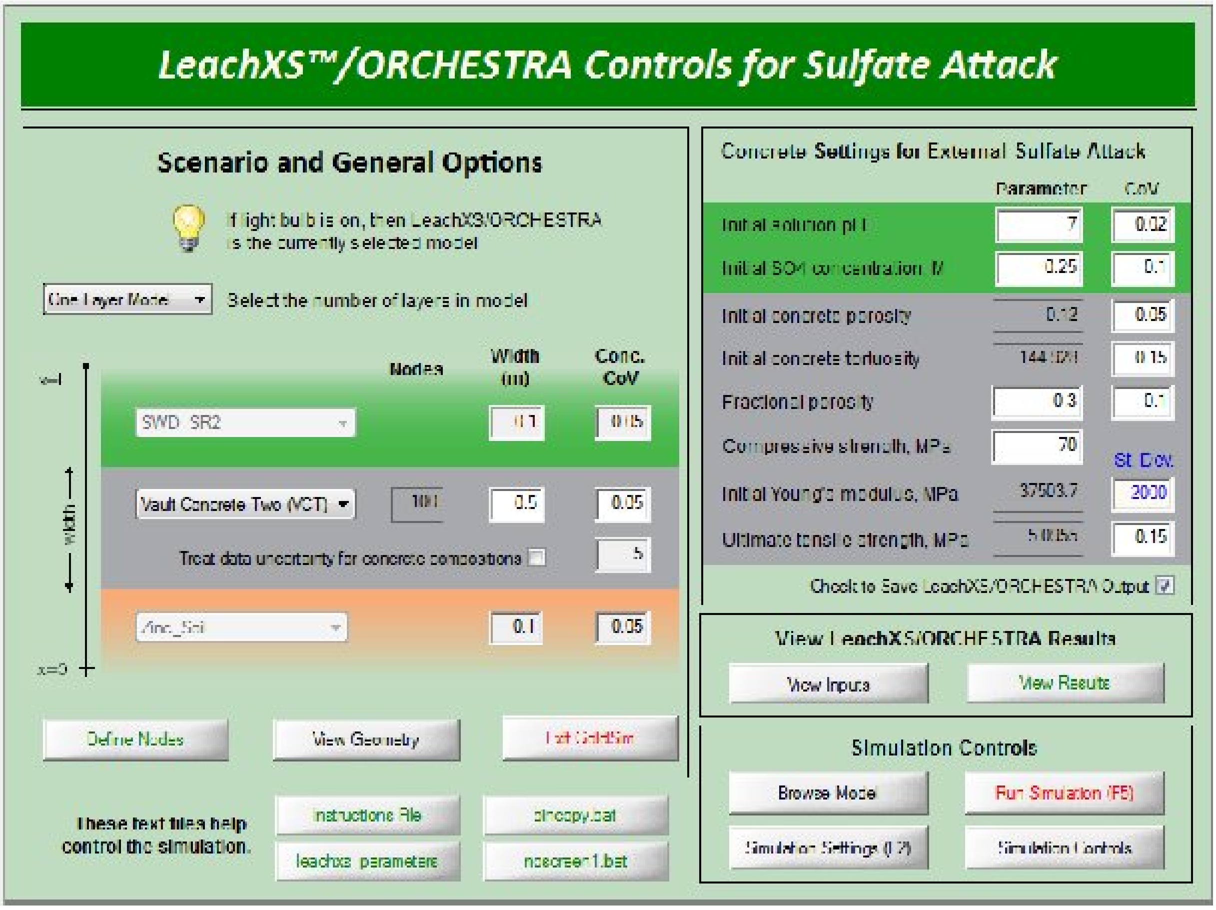

Fig. 7. Dashboard to Control the LeachXS™/ORCHESTRA Sulfate Attack Model

When the LeachXS™/ORCHESTRA model is selected from the GoldSim Dashboard, LeachXS™/ORCHESTRA is called using the CBP custom DLL that uses the input generated from the Dashboards to run the model. After the run completes, the results generated by STADIUM® are retrieved by GoldSim using the CBP custom DLL. LeachXS™/ORCHESTRA model results can be viewed using a set of pre-defined graphs (resembling that in Fig. 5).

CARBONATION MODELING USING LEACHXS™/ORCHESTRA

The penetration of gaseous carbon dioxide within partially saturated concrete can initiate a series of carbonation reactions with both dissolved ions and the hydrated cement paste. The carbonation process does not necessarily have a negative effect on the properties of the cement and can prove beneficial. However, carbonation has been shown to increase constituent leaching for certain pH-sensitive species and can have a detrimental effect on reinforced concrete structures by lowering pH to ca. 9 and depassivating embedded steel accelerating corrosion that can result in cracking and increased contaminant release and transport.

The potentially negative impacts of carbonation are important to HLW tank integrity and closure evaluations. The CBP Software ToolBox provides a simplified LeachXS™/ORCHESTRA model (Fig. 2) of a HLW tank integrity scenario that focuses on constituent leaching and pH changes resulting from carbonation (coupled with constituent leaching). The GoldSim Dashboard for controlling the LeachXS™/ORCHESTRA simulation is similar to that shown for sulfate attack in Fig. 7. The user has the ability to vary the partial pressures of carbon dioxide and oxygen (e.g., representing varying conditions in soil contacting concrete). Subsequent carbonation models are planned that will include pore filling and resulting changes in transport properties (that will be implemented in a fashion similar to LeachXS™/ORCHESTRA sulfate attack model).

CONCLUSIONS

The Cementitious Barriers Partnership (CBP) Project has developed a set of integrated modeling tools and leaching test methods to help improve understanding and prediction of the long-term performance of cementitious materials used in nuclear applications. State-of-the-art modeling tools, namely LeachXS™/ORCHESTRA and STADIUM®, were selected for their demonstrated abilities to simulate reactive transport and degradation in cementitious materials. The models have been linked to a GoldSim Monte Carlo simulator using a consistent interface to better characterize model uncertainties and as a means to coupling the models to provide more accurate predictions.

Two important degradation scenarios were selected for initial demonstration: sulfate ingress / attack and carbonation of cementitious materials. Sulfate attack of a concrete can cause cracking that significantly changes the transport and structural properties of the concrete. Carbonation has been shown to increase leaching of some constituents and can potentially have a detrimental effect on reinforced concrete structures by significantly lowering pH and depassivating embedded steel (e.g. rebar) and accelerating corrosion. These are important processes related to low-activity waste disposal and high-level waste tank integrity and closure evaluations. The chemical and physical components in the STADIUM® and LeachXS™/ORCHESTRA models can be used as part of a larger scale release scenario supporting environmental impact assessments.

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