Software Quality Assurance for LeachXS/ORCHESTRA as a Tool for Assessment of Waste Management Systems Performance - 17486

K.G. Brown[1], D.S. Kosson[1], H.A. van der Sloot[2], P. Seignette[3], and J.C.L. Meeussen[4]
[1]Vanderbilt University, Dept. of Civil and Environmental Engineering, Nashville, TN
[2]Hans van der Sloot Consultancy, Langedijk, The Netherlands
[3]Energy Research Centre of The Netherlands (ECN), Petten, The Netherlands
[4]Nuclear Research and Consultancy Group (NRG), Petten, The Netherlands

ABSTRACT

Qualified modeling and simulation tools and experimental data are needed to provide a reasonable basis for the incorporation of realistic wasteform retention assumptions (i.e., those without orders-of-magnitude conservatism) into performance assessments and regulatory decisions. Use of highly conservative assumptions in performance assessments has historically led to the overprediction of release and near-field transport by as much as 4- to 6-orders of magnitude thereby limiting the nature and quantities of certain contaminants of concern in near surface disposal facilities. This project provides peer-reviewed models and characterization methods to provide more reasonable assumptions for use in performance assessments and regulatory decisions. Simulations tools have been developed to predict hydraulic and chemical performance of wasteforms and barriers used in nuclear applications under several important aging and degradation scenarios, including sulfate attack, carbonation, oxidation, cracking, and leaching; these tools are complaint with DOE Order 414.1D and ASME NQA-1. Wasteform characterization methods have been developed that are consistent with US EPA's Leaching Environmental Assessment Framework (LEAF) currently part of EPA's Hazardous Waste Test Methods (SW-846); the resulting experimental data are evaluated using LeachXS. ORCHESTRA models, that can be called seamlessly from LeachXS, have been developed representing both laboratory and field conditions; these models have undergone an extensive Software Quality Assurance process where they have been calibrated (where necessary), verified, and validated to be compliant with relevant guidelines. The models used for field predictions have also been incorporated into the Cementitious Barriers Partnership (CBP) Software Toolbox that allows probabilistic evaluation of field scenarios. The foci over the next year will be on providing 1) a mechanistic basis for projecting the retention of Tc-99, I-129, and other

important radionuclides in near-surface disposal facilities at the Savannah River and Hanford Sites and 2) a technical basis for assessing the efficacy of macro-encapsulation of mercury-contaminated debris at the Oak Ridge Reservation.

INTRODUCTION

Qualified modeling tools and data are necessary to provide a defensible basis for incorporating realistic wasteform retention assumptions into performance assessments (PAs) and regulatory decision making. The use of highly conservative assumptions in PAs has led to overpredicting release from cementitious materials and near-field transport by several orders of magnitude that also limits the nature and quantities of contaminants of concern that can be disposed of in near surface disposal facilities. Chemical equilibrium, or speciation, models are useful for estimating the distribution of constituents, including radionuclides and hazardous chemicals, over different physicochemical forms and phases in a chemical equilibrium systems representing wasteforms and barriers used in waste nuclear applications. ORCHESTRA (Objects Representing CHEmical Speciation and TRAnsport) is a general software modeling framework for solving chemical equilibrium and reactive transport problems in the waste management arena [1-3].

Recently, the Cementitious Barriers Partnership (CBP) has been moving from a focus on developing integrated tools, including the use of ORCHESTRA for reactive transport simulations for cementitious waste forms, to the application of tools in U.S. Department of Energy (DOE) PAs including that for the Savannah River Site (SRS) Saltstone Disposal Facility (SDF) [4, 5] and potential application to the Hanford Site Integrated Disposal Facility (IDF). In light of this new direction, the CBP team recently reevaluated its software Quality Assurance/Quality Control (QA/QC) documentation to assure that it aligns with both NQA-1 [6] and DOE Order 414.1D (entitled *Quality Assurance*). The outcome of this reevaluation was that CBP software tools including ORCHESTRA, which has been used to support DOE PAs, required additional verification test cases and confidence building (“validation”) in a form more amenable to review and reference to support DOE PAs.

This paper summarizes verification and validation of selected ORCHESTRA functionality and models for use in DOE waste management applications.

ORCHESTRA verification test cases range from simple cases using analytical results to more complex cases using "code-to-code" comparisons, including international benchmarking studies [7, 8]. Components are included in verification cases that are important to modeling reactive transport systems, including chemical equilibrium and transport (e.g., diffusion). Current "validation" test cases include two important aging mechanisms for U.S. DOE applications: 1) sulfate attack relevant to salt waste disposal at the SDF at the Savannah River Site and 2) carbonation relevant to waste tank closure at the Hanford Site. Additional test cases are available (e.g., laboratory 3-dimensional monolith diffusion) and others will subsequently be added as needed to build confidence in the use of ORCHESTRA for modeling relevant waste disposal applications. For this paper, "validation" of the carbonation model will be of primary focus.

THE ORCHESTRA MODELING FRAMEWORK

In contrast with existing standard geochemical codes such as PHREEQC [9], Geochemist's Workbench (GWB) [10], MINTEQA2[11], and ECOSAT [12], the chemical and physical model equations in ORCHESTRA are not precompiled in source code but instead are specified in separate text files that are "interpreted" (or compiled) by the ORCHESTRA calculation kernel at run time. This approach makes model definitions transparent and available to end-users. The object-oriented structure of ORCHESTRA makes it relatively easy to define new models and new model functionality using existing models. This approach provides a strict separation between model definitions and the ORCHESTRA calculation kernel, meaning that new functionality can be added without changing and recompiling the calculation kernel. As such the kernel remains simple and efficient.

The ORCHESTRA object-oriented structure serves as a versatile framework for implementing chemical equilibrium models. The framework consists of three basic object types (i.e., "entities", "reactions", and "phases") that form the foundation from which models are composed in a hierarchical manner [3]. This hierarchical approach ensures consistent and compact model definitions and has been used to implement a number of widely used chemical models, such as aqueous complexation, activity correction, precipitation, surface complexation and ion exchange, and several more sophisticated adsorption models including electrostatic interactions, NICA, and CDMUSIC. The verification of the basic chemical equilibrium functionality will be briefly described.

ORCHESTRA models can also incorporate transport processes (e.g., diffusion and advection) using finite difference solution schemes [2, 3] where verification of the diffusion solution based on an analytical solution is briefly summarized in this paper. In general, basic transport model components are developed by the CBP team and then integrated with other elements for specific higher-level applications, including carbonation, sulfate attack, and percolation (for cracked cementitious materials). These higher-level models are then available for download from LeachXS™, a database/expert decision support system for characterization and environmental impact assessment based on estimated contaminant release derived from leaching tests [13, 14].

VERIFICATION OF A SIMPLE CHEMICAL EQUILIBRIUM SYSTEM

The first verification test case demonstrates the ability of ORCHESTRA to solve a simple chemical equilibrium system. The simple system in this test case represents the speciation of carbonate in water as a function of pH and is composed of two independent chemical components, CO_3^{-2} and H^+, and is specified by three chemical reactions. For this case, the chemical reactions are taken from the Minteq V4 thermodynamic database file[1].

For this test case, results could be obtained using a number of chemical equilibrium solver programs. For this case, Appelo's Notepad++ interface to PHREEQC version 3[2], or a “code-to-code” type comparison, was used. A set of 11 solutions were defined where the carbonate concentration was set to 1 mmol/liter (or 0.001 M), the temperature to 25ºC, and the pH was varied from 2 to 12 (in increments of 1 pH unit). Fig. 1 shows excellent agreement among the ORCHESTRA and PHREEQC results.

[1] The database used is obtained from http://www2.epa.gov/exposure-assessment-models/minteqa2. The ORCHESTRA version of this database can be found at: http://www.meeussen.nl/orchestra/minteqv4.txt.
[2] PHREEQC [9] is widely used to simulate various geochemical processes. Available at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/ (16 December 2016).

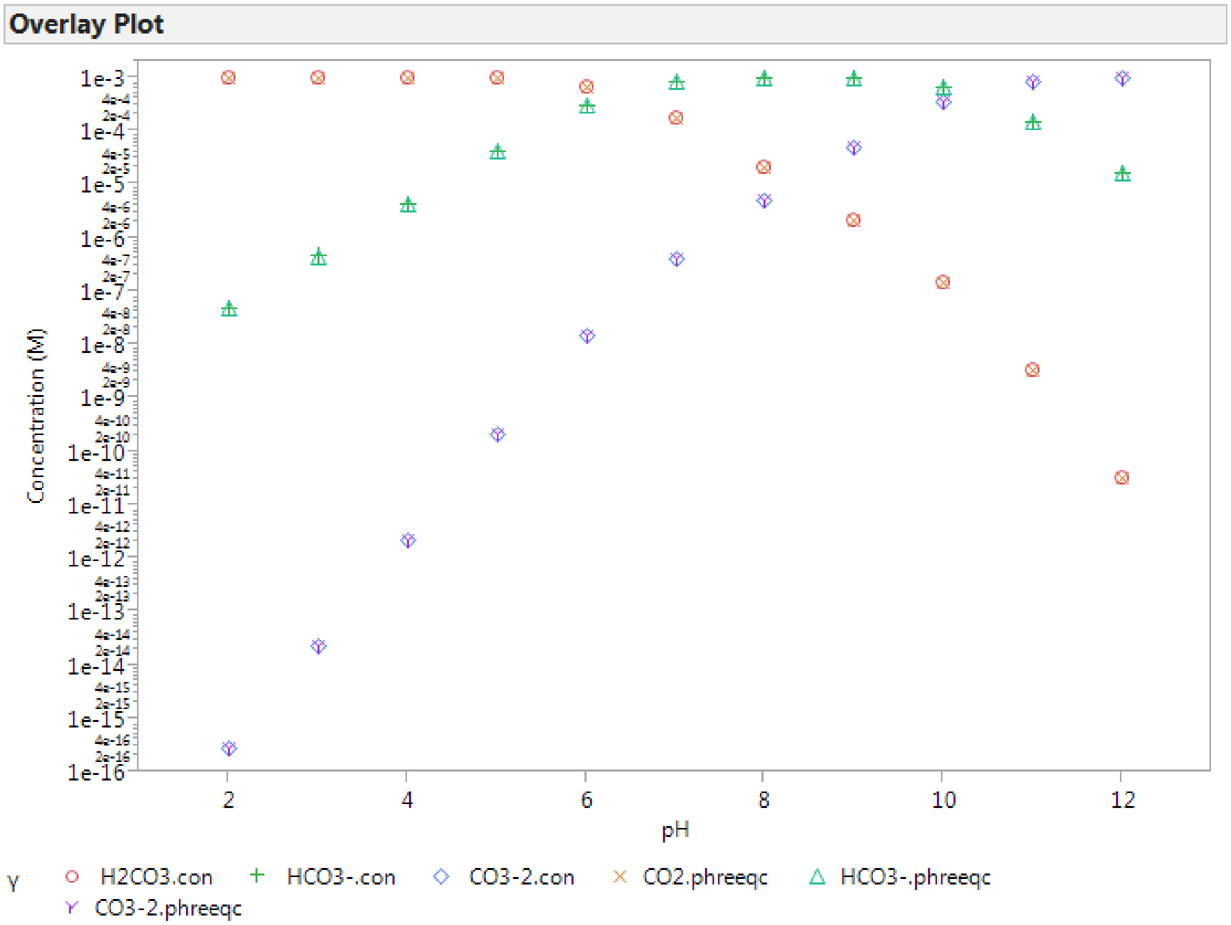

Fig. 1. Comparisons of ORCHESTRA and PHREEQC Results for a Simple Chemical Equilibrium System.

VERIFICATION OF TRANSPORT: DIFFUSION

This test case is used to demonstrate that ORCHESTRA can be used to solve a system involving diffusion of a non-reactive tracer that undergoes first-order (in this case, radioactive) decay. The equilibrium system in this example represents four primary entities (i.e., I-129, Tc-99, Th-232, and U-235) but no chemical or mineral reactions. All species can be considered non-reactive tracers undergoing only diffusion and radioactive decay for this test case.

For this test case, the Nuclear Energy Agency (NEA) Thermochemical Database (TDB) Project[3] reactions (converted to first PHREEQC and then ORCHESTRA format) were used. A user-defined database with bulk

[3] https://www.oecd-nea.org/dbtdb/

adsorption reactions was also developed to represent linear sorption (*R* or K_d approach) as is often used in US DOE PA models.

Because the constituents of interest in this test problem are non-reactive tracers undergoing radioactive decay (and no other reactions), an analytical expression is available to calculate the concentration, $C(x,t)$, at a given location, *x*, and time, *t* [15]:

$$C(x,t) = \frac{C_0}{\sqrt{\frac{4\pi Dt}{R}}} exp\left[-\left(\frac{x^2}{\frac{4Dt}{R} - \lambda t}\right)\right] \quad \text{(Eq. 1)}$$

where C_0 is the initial concentration throughout the material, *D* is the diffusion coefficient, *R* is the retardation factor, and λ is calculated ($\lambda = \ln(2)/t_{½}$) from the half-life, $t_{½}$ (sec), of the isotope. The ORCHESTRA results (Fig. 2) are compared to those from the corresponding analytical expression (Eq. 1) for Tc-99. Note that the ORCHESTRA Tc-99 results (at times where results exceed the 1e-13 value used to approximate zero in ORCHESTRA [2]) are in excellent agreement to those from the analytical expression[4].

[4] Agreement is generally excellent for all isotopes considered although there is a divergence for the I-129 values (from the analytical expression) at simulated times exceeding 2E+07 years due to the small amount of adsorbed I-129 used to represent the K_d relative to the unretarded specie (i.e., *R* = 1 in Eq. 1).

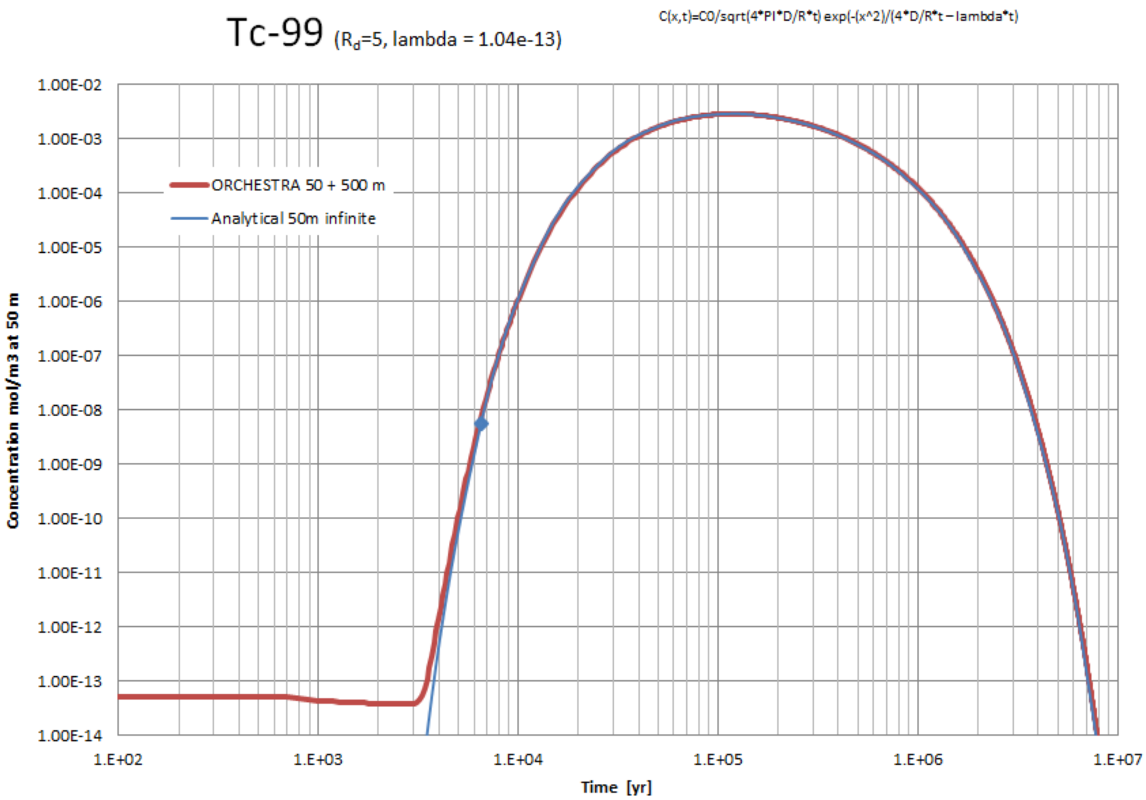

Fig. 2. Comparison of Tc-99 Results for Verification Test Problem 3

VERIFICATION AND VALIDATION OF CARBONATION

An important challenge for the U.S. DOE is how to assess the integrity of closed waste tanks that previously stored millions of gallons of highly radioactive wastes [16]. Many of these tanks are decades past their design lives, have leaked or were overfilled, and must be emptied of waste and closed to satisfy regulatory agreements. Carbonation-induced corrosion (that could result in rebar corrosion, cracking, and ultimately increased release of contaminants) has been identified as a primary degradation and potential failure mechanism for DOE waste tanks; these tanks may be largely empty for many years prior to closure. The performance of the closed tank over centuries, if not millennia, must be assessed to evaluate the potential for residual radionuclides in the tanks to be released and adversely impact human health and the environment. This sections evaluates prediction from the ORCHESTRA carbonation model relative to both an analytical solution (verification) and the measured carbonation depth in a dome core sample from a buried tank in the Hanford Waste Management Area (WMA) C Tank Farm.

Verification

The carbonation model previously used to evaluate tank closure [16] was extensively modified to include oxidation and a new finite difference approach to solving diffusion allowing a range from fully explicit to fully implicit solution. Because of the extensive changes to the transport solution scheme, it was decided to verify the new carbonation-oxidation transport solution and corresponding model. Results computed in the carbonation model are verified using an analytical solution entitled *Diffusion from a stirred solution of limited volume* [17] where a solute is diffusing from a well-mixed solution of limited volume into an infinite sheet of uniform material.

The sheet of thickness $2L_{sheet}$ occupies a space $-L_{sheet} \leq x \leq L_{sheet}$, while the solution of limited extent occupies the spaces $-L_{sheet} - L_{solution} \leq x \leq -L_{sheet}$, $L_{sheet} \leq x \leq L_{sheet} + L_{solution}$. The concentration of the solute is uniform and initially C_0 and the initial concentration in the sheet is zero. The solution for the fraction (M_t/M_∞) of solute in the sheet at time t as a fraction of the amount after infinite time (M_∞) is [17]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} exp\left(-\frac{D q_n^2 t}{L_{sheet}^2}\right) \qquad \text{(Eq. 2)}$$

where $\alpha = V_{solution}/(KV_{sheet})$ (where K is the partition factor) or the ratio of the volumes of solution and sheet (weighted by the partition coefficient) and the q_n's are the non-zero positive roots of: $\tan(q_n) = - q_n$.[5]

For this test case scenario (diffusion from a tank solution into a porous monolith), the concentration (C/C_∞) in the sheet at a given distance (x) from the boundary and time t relative to the concentration (C_∞) at infinite time is given by [17]:

$$\frac{C}{C_\infty} = 1 + \sum_{n=1}^{\infty} \frac{2(1+\alpha) exp\left(-\frac{D q_n^2 t}{L_{sheet}^2}\right)}{1+\alpha+\alpha^2 q_n^2} \frac{cos\left(\frac{q_n x}{L_{sheet}}\right)}{cos(q_n)} \qquad \text{(Eq. 3)}$$

where

[5] Because α may vary and differ from available values (e.g., Table 4.1 [17]), a Matlab function was developed to compute roots where the first six roots were computed at the α values given by Crank [17] and were the same as those provided in the reference. Various results estimated using Eq. 2 for the fractional uptake were also compared to those in Fig. 4.6 [17] and found to be in agreement.

$$C_\infty = \left(\frac{2V_{solution}}{2V_{sheet}} \frac{C_0}{1+\alpha}\right) = KC_0\left(\frac{\alpha}{1+\alpha}\right) \qquad \text{(Eq. 4)}$$

and ($V_{solution}/V_{sheet}$) = $K\alpha$. Results computed from Eq. 3 and Eq. 4 were compared to those from the ORCHESTRA carbonation model for a conservative tracer (in this case, Br-) over 180 days as illustrated in Fig. 3. The agreement is excellent for significant tracer concentrations [2].

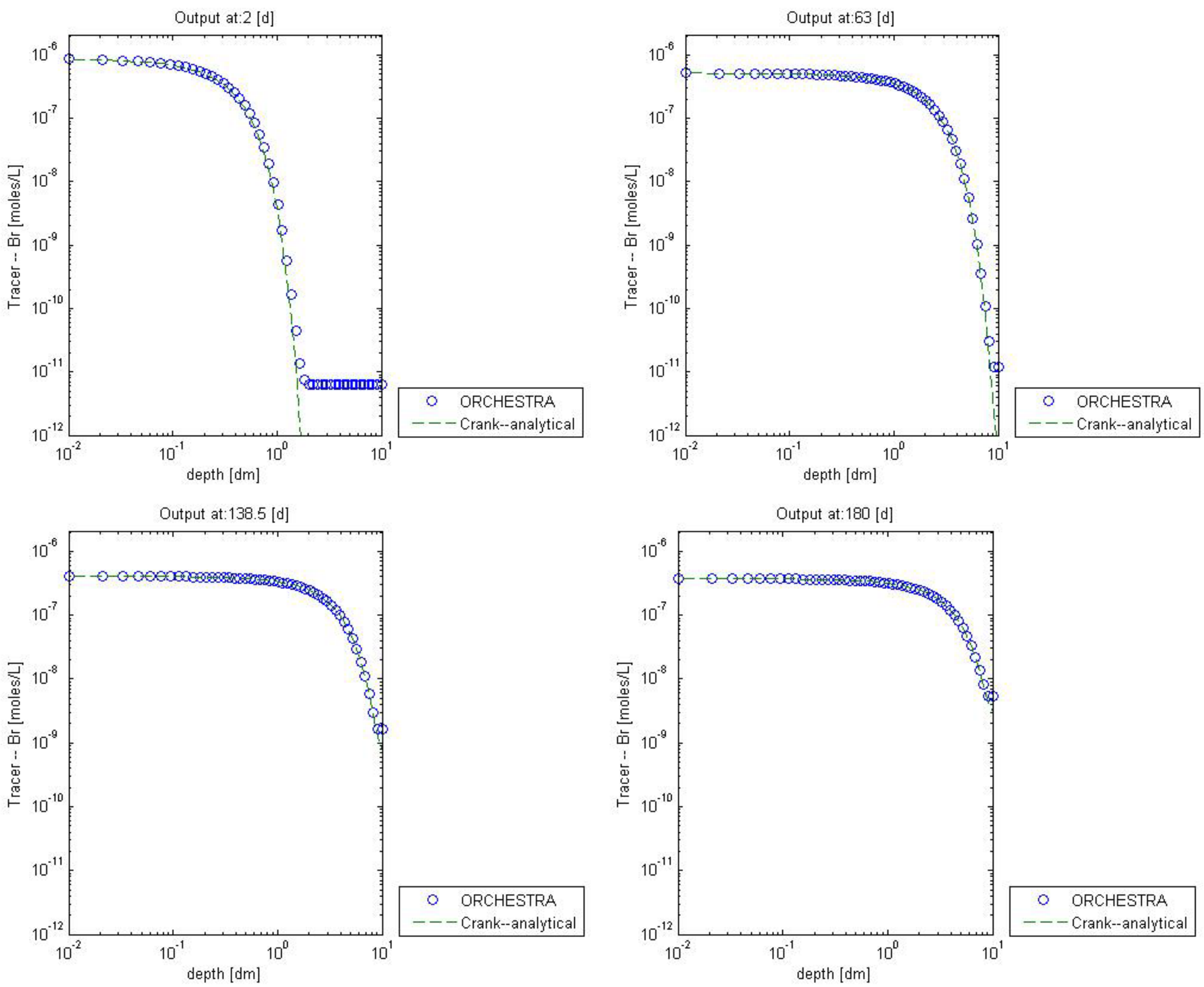

Fig. 3. Comparison of Analytical (dashed line) and ORCHESTRA (blue circles) for a non-reactive tracer (Br-) with initial tank concentration of $1\text{x}10^{-6}$ M.

Building Confidence in the Model Prediction (a.k.a., "Validation")

In December 2010, a 1.4-m (55-inch) diameter core of reinforced concrete was removed from the dome of Hanford waste tank 241-C-107 [18]. The 241-C-107 tank was constructed in the 1944-45 time frame [19] and thus was buried for approximately 65 years before the core was removed. The depth of carbonation (assumed measured using phenolphthalein at pH approximately 10) was shallow, approximately 0.001-0.002 m (0.04 to 0.08 in.) from the top surface [20].

To build confidence in ORCHESTRA carbonation model predictions (often referred to as “validation”), an ORCHESTRA model was developed to predict carbonation depth for a scenario representative of the 241-C-107 waste tank dome core sample. The model was not calibrated to better predict measured results. The ORCHESTRA results for pH (related to carbonation) and *pe* (related to oxidation[6]) as a function of depth into the material after 65 years are shown in Fig. 4. The predicted depth (where pH ≤ 10) of 0.002 m in 65 years for a dome core from the Hanford 241-C-107 waste tank [20] appears to agree very well with the measured value, considering uncertainties in field conditions and likely differences among assumed and actual transport parameters.

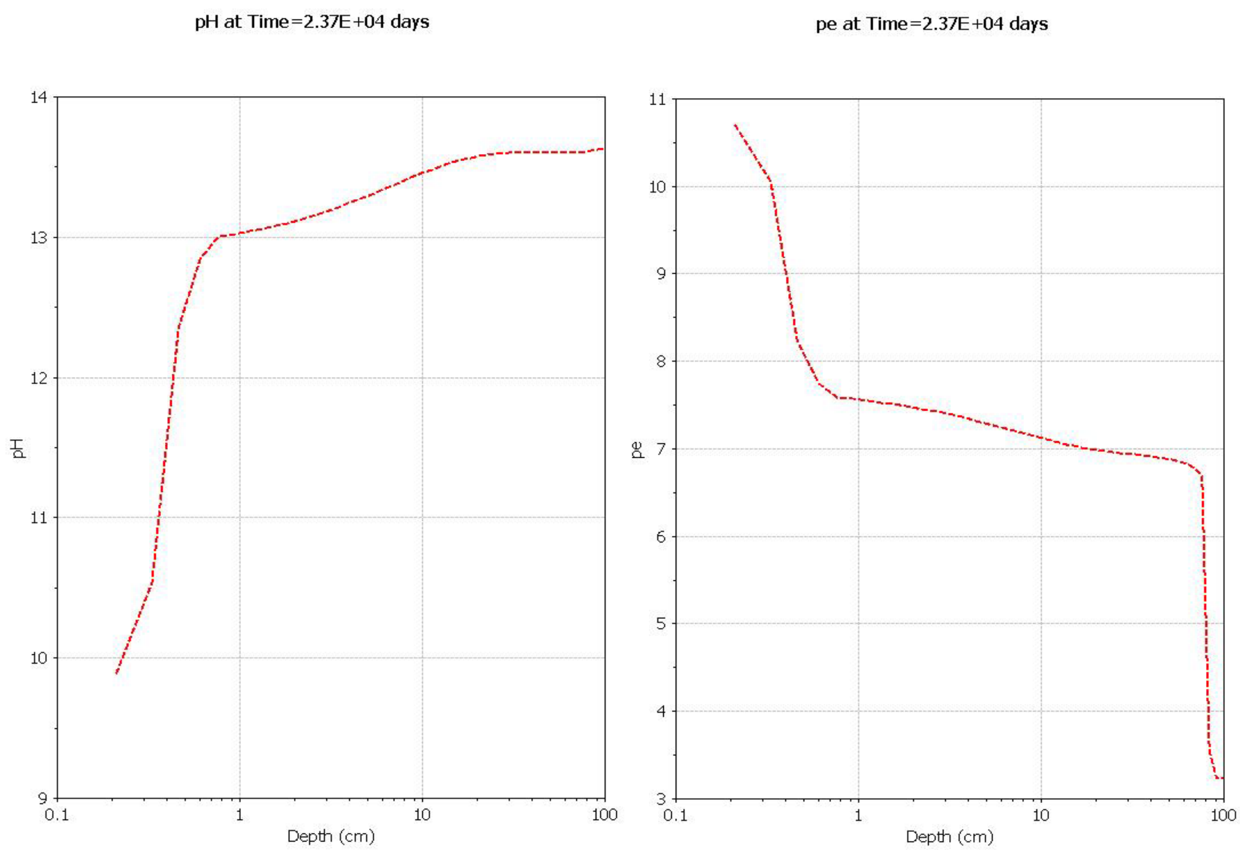

Fig. 4. Results from the ORCHESTRA Carbonation-Oxidation model representing the Hanford 241-C-107 Tank Dome Core Sample.

[6] The verification and validation of the ORCHESTRA *pe* predictions are current projects.

CONCLUSIONS

The verification and “validation” of several ORCHESTRA models important to supporting U.S. DOE performance assessments (PAs) are summarized. The ORCHESTRA chemical equilibrium model show exact agreement with the widely used USGS PHREEQC model. The diffusion and radioactive decay schemes implemented in ORCHESTRA agree well with the corresponding analytical solution for significant concentrations (i.e., those exceeding the value of 1e-13 M used in ORCHESTRA to represent zero). The verification and “validation” of the newly revised carbonation model was summarized demonstrating the ability of the model to reproduce the appropriate analytical solution as well as predict the carbonation depth for a representative Hanford waste tank closure scenario. These results support the use of CBP models to build confidence in U.S. DOE performance assessment for cementitious waste forms in shallow land burial.

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DISCLAIMER

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