A Dual Regime Reactive Transport Model for Simulation of High Level Waste Tank Closure Scenarios – 13375

Sohini Sarkar[1], David S. Kosson[1], Hans Meeussen[2], Hans van der Sloot[3],
Kevin Brown[1], Andrew C. Garrabrants[1]
Consortium for Risk Assessment with Stakeholder Participation (CRESP)
[1] Vanderbilt University, Nashville, TN, USA
[2] Nuclear Research and Consultancy Group, Petten, The Netherlands
[3] Hans van der Sloot Consultancy, The Netherlands

ABSTRACT

A numerical simulation framework is presented in this paper for estimating evolution of pH and release of major species from grout within high-level waste tanks after closure. This model was developed as part of the Cementitious Barriers Partnership. The reactive transport model consists of two parts – (1) transport of species, and (2) chemical reactions. The closure grout can be assumed to have varying extents of cracking and composition for performance assessment purposes. The partially or completely degraded grouted tank is idealized as a dual regime system comprising of a mobile region having solid materials with cracks and macropores, and an immobile/stagnant region having solid matrix with micropores. The transport profiles of the species are calculated by incorporating advection of species through the mobile region, diffusion of species through the immobile/stagnant region, and exchange of species between the mobile and immobile regions. A geochemical speciation code in conjunction with the pH dependent test data for a grout material is used to obtain a mineral set that best describes the trends in the test data of the major species. The dual regime reactive transport model predictions are compared with the release data from an up-flow column percolation test. The coupled model is then used to assess effects of crack state of the structure, rate and composition of the infiltrating water on the pH evolution at the grout-waste interface. The coupled reactive transport model developed in this work can be used as part of the performance assessment process for evaluating potential risks from leaching of a cracked tank containing elements of human health and environmental concern.

INTRODUCTION

Cementitious materials are often used to stabilize the residual radioactive wastes [1, 2]. The cement grout is expected to act as a hydraulic and physical barrier for the waste materials. However, physical and chemical processes leading to cracking of the cement grout can significantly alter the amount of contaminants leached from the tank. In estimating source term parameters from residual waste in high level waste tanks after closure, it is generally assumed that the tank integrity degrades over time and the release occurs through dissolution of contaminants into the infiltrating water flowing through cracks in the grout within the tank [3]. Various release models were investigated in the past to simulate the release of contaminants from

the high-level waste forms [4] such as adsorption-controlled release, solubility-controlled release, linear release, and diffusion controlled release. The fate and transport of contaminants released from the tank was found to be strongly related to the pH of the water as it migrates through the tank grout [5]. However, the waste pH is dependent on the chemical behavior and pore solution pH of the cementitious grout used for stabilization of the waste, crack state and consequently contact time of the infiltrating water with the grout matrix.

A numerical framework is presented in this paper to simulate the pH evolution and release of major species through the degraded (i.e., cracked) cementitious grout used for closure of high level waste tanks. The mineralogical characteristics of the grout material were first identified by assessing various mineral sets in describing its pH dependent behavior. Then a dual regime transport model (identified as a potential conceptual model for describing cracked concrete in [1]) coupled with chemical reactions was implemented to simulate leaching of species through mobile region with cracks and macropores (faster pathway) and solid matrix with micropores (slower pathway). The model predictions were compared with an up-flow column percolation test data performed on size reduced grout material that is representative of the cracked material. Most of the long-term performance tests span for a few years. However, the assumptions made on the physical and hydraulic properties of the tank grout spans over hundreds of years [3, 6]. The dual regime reactive transport model and the up-flow column percolation test outputs were estimated as a function of liquid-to-solid ratio, which generally translates into hundreds of years of leaching time depending on infiltration rate, depth through which infiltration occurs, and density of the material. The model can be evaluated against short-term test data and used to provide estimates of risks from leaching from grout and residual waste within a tank after closure. Finally, the effects of the crack state and the infiltrations rates on the pH evolution and release of major species are shown using the coupled dual regime reactive transport model.   It is important to recognize that ingress and reaction of carbon dioxide from the atmosphere can result in further decreases in pH (typically to pH ~9) than considered in this model but also will be limited by significant resistance by cover materials to ingress.

MATERIAL DESCRIPTION

The material chosen for this study is a ternary blend cement mortar analogous to the materials used as backfill/infill applications [7]. It comprises of Type I/II Portland cement, grade 100 blast furnace slag, and class F fly ash. The water to binder ratio is 0.38 and the mortar contains quartz sand at a volume replacement level of 54%. The mixture proportions are given in Table 1.

Table 1. Mixture proportions for the cement grout after [7].

Ingredients	Mass %
Type I/II cement (ASTM C 150)	5.88
Grade 100 blast furnace slag (ASTM C 989)	13.48
Type F fly ash (ASTM C 618)	6.62
Quartz sand (ASTM C 33)	62.25
Water (maximum)	11.76

AQUEOUS-SOLID PARTITIONING DATA

The size reduced grout material was subjected to a pH dependence test [8–10] (USEPA Method 1313) for assessment of its behavior under varying pH conditions. This is an equilibrium-based leaching test designed to provide aqueous extracts representing the liquid-solid partitioning (LSP) curves of constituents as a function of eluate pH. This parallel batch procedure consists of nine extractions at targeted pH values and one extraction at the natural (own) pH of the material at room temperature ($21\pm2\ ^0$C) [8]. The solid material is particle-size reduced to facilitate the approach to solid-liquid equilibrium. Dilute nitric acid or base (sodium or potassium hydroxide) in deionized water with a final L/S of 10 mL/g-dry is used to achieve final extract pH values at specified target values ranging between 1 and 13. Eluate concentrations for constituents of interest are plotted as a function of eluate pH allowing for comparison to quality control and assessment limits. Results also provide a pH titration curve for each material. Results for a wide range of materials, test conditions and constituents have been compiled in a LeachXS[1] database [12–14] and the test results for the grout material used in this study were drawn from the LeachXS compilation.

GEOCHEMICAL SPECIATION MODELING

The geochemical speciation code, ORCHESTRA [15] (also embedded in LeachXS), was used to simulate the leaching behavior of the grout material evaluated in this paper. The chemical reaction equations were written in terms of the selected primary species $Al^{+3}, Ca^{+2}, Fe^{+3}, Mg^{+2}, H_4SiO_4, SO_4^{-2}, H_2CO_3$ and H^+. The simulations were performed by including all aqueous complexes available for these components, and mineral phases chosen from the MINTEQ and CEMDATA 2007 databases [16, 17]. The activity coefficients were calculated using Davies' equation [18] at room temperature ($25\ ^0$C). All mineral precipitation dissolution reactions were assumed to be under local equilibrium conditions. After comparing calculated dissolved concentrations with measured total dissolved concentrations, a mineral set (i.e., a set of precipitation-dissolution reactions) was selected that gave the best description of the total dissolved concentrations. The inputs to the ORCHESTRA geochemical speciation model

---

[1] LeachXS is a database/expert decision support system for characterization and environmental impact assessment based on estimated contaminant release as derived from leaching tests. The databases are available through the Cementitious Barriers Partnership project website [11].

were - the initial available/reactive concentrations of the components, and the final pH of the solution in which the samples were immersed. The initial available concentrations of the components were estimated by selcting the maximum leached amount of each component within the pH range of 1 to 13. These values were assumed to be the maximum amounts available for chemical reactions and less than or equal to the total amounts present in the system. The model calculates the liquid-solid equilibrium phases given the set of minerals present in the system and calculates the total dissolved amounts of the components at different pH conditions. A set of 17 minerals was chosen (Table 2) as the model set by comparing the simulation results with the test data. Among these minerals, calcium silicate hydrate was modeled as a combination of two concurrent solid solution systems [17, 19]– (i) mixture of amorphous silicon dioxide and Tobermorite-I and (ii) mixture of Jennite and Tobermorite-II. The rest of the minerals were treated as pure phases. The model predictions and test data of total dissolved concentrations of six components (i.e., Al, Ca, Fe, Mg, Si and S) are shown in Figure 1. It is important to mention that a good model prediction could not be achieved for silicon (Si) in the low pH region (pH < 7) using several combinations of mineral phases including the combinations recommended for cementitious materials in the literature [17, 20, 21]. A possible explanation would be that at low pH range the Si concentration is not determined by equilibrium but by slow reaction kinetics, which was not included in the current model formulation, or the lack of appropriate literature data on Si behavior in the acidic pH range. However, the deviation at low pH does not affect the calculations in the alkaline pH range. However, the lowest pH observed in low-pH cements is around pH 9 [23, 24] and remains about pH 7 even after carbonation. Therefore, the deviation in the Si model predictions for pH < 7 was not addressed in this paper. However, the model reproduced the trends in the behavior of the other components over the whole pH domain.

Table 2. Mineral set chosen for geochemical speciation modeling [16, 17].

| Mineral Phase	Expanded Formula	Common Name	$\log_{10}K_{sp}$
$C_6A\bar{S}H_{32}$	$6CaO.Al_2O_3.32H_2O$	Ettringite	-57.00
C_3AH_6	$3CaO.Al_2O_3.6H_2O$	Hydrogarnet	-79.53
C_3FH_6	$3CaO.Fe_2O_3.6H_2O$	Fe-Hydrogarnet	-72.41
C_2ASH_8	$2CaO.Al_2O_3.SiO_2.8H_2O$	Stratlingite	-49.44
C_2FSH_8	$2CaO.Fe_2O_3.SiO_2.8H_2O$	Fe-Stratlingite	-42.33
$C_{1.67}SH_{2.1}$	$1.67CaO.SiO_2.2.1H_2O$	Jennite	-29.42
CH	$CaO.H_2O$	Portlandite	-22.80
$C\bar{S}H_2$	$CaO.SO_3.2H_2O$	Gypsum	4.60
Al(OH)$_3$ (amorphous)	-	Gibbsite	-7.76
$C_2S_{2.4}H_{3.2}$	$2CaO.2.4SiO_2.3.2H_2O$	Tobermorite-I	-28.03
$C_{0.83}SH_{1.3}$	$0.83CaO.SiO_2.1.3H_2O$	Tobermorite-II	-11.26
SiO_2	-	Silica	2.71
Fe(OH)$_3$ (microcrystalline)	-	Ferric Hydroxide	-3.00
$Mg(OH)_2$	-	Brucite	-16.84
$CaO.CO_2$	-	Calcite	-7.20
M_4ACH_9	$4MgO.Al_2O_3.CO_2.8H_2O$	CO$_3$-Hydrotalcite	-67.53
MC	$MgO.CO_2$	Magnesite	-7.32
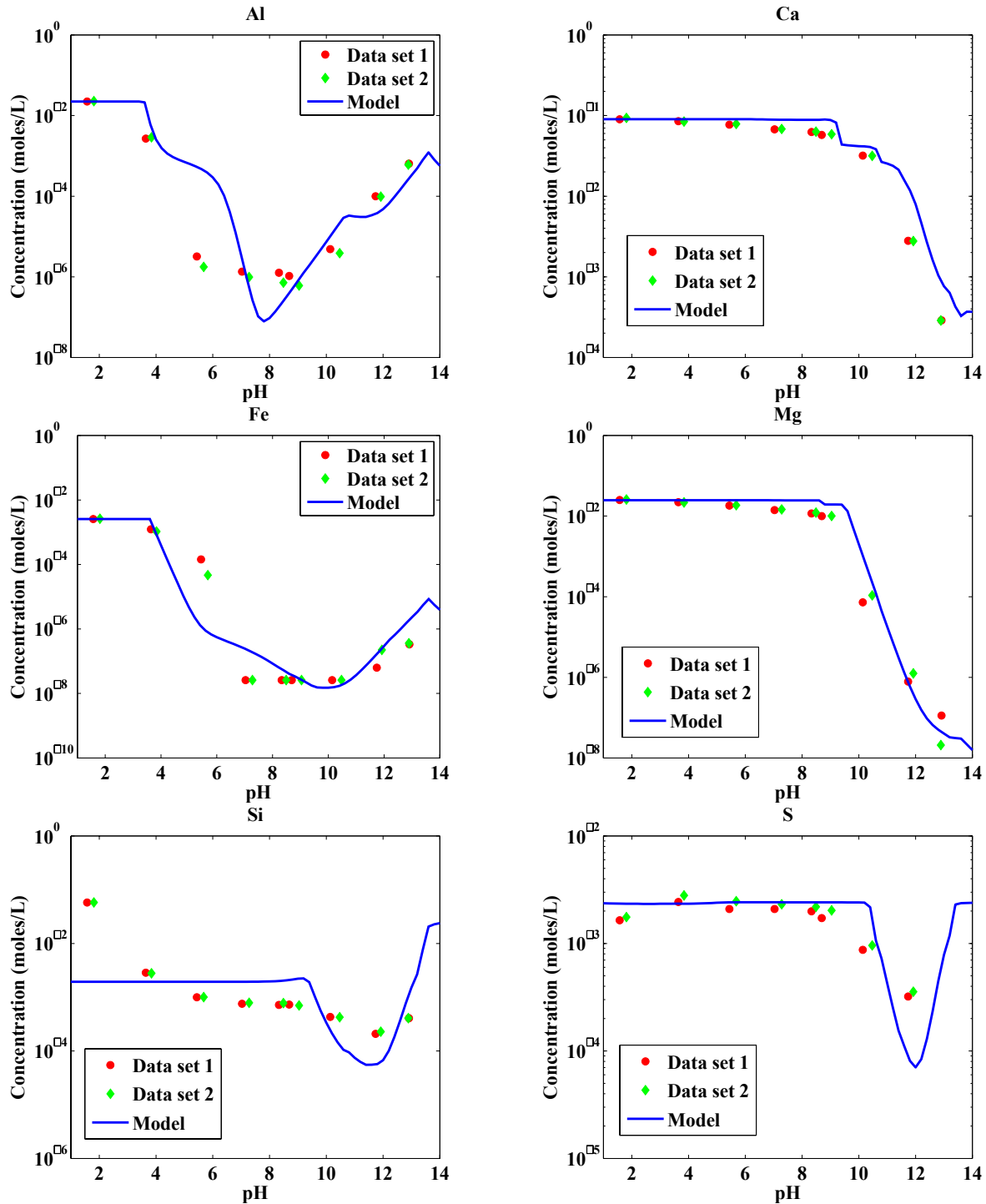
Figure 1. Comparisons of model predictions with the pH dependence test data (Method 1313 in duplicate).

After selection of a mineral set that represented the overall behavior of the material, an up-flow column test was conducted to assess leaching through the material under percolation conditions. A coupled dual regime reactive transport model was then implemented to simulate the column percolation test and the model predictions were compared with the test data.

6

UP-FLOW COLUMN PERCOLATION DATA

USEPA Method 1314 is an up-flow column percolation method [10, 25, 25] designed to provide the liquid-solid partitioning of inorganic constituents (e.g., metals, radionuclides) and non-volatile organic constituents (e.g., dissolved organic carbon) in a granular solid material as a function of liquid-to solid ratio (L/S) under percolation conditions. For this test method, the solid material is size reduced by crushing to 85 percent less than 2.5 mm. The first eluates of the column test provide insight into initial pore solution composition either in a granular bed (e.g., soil column) or in the crack/pore space of low-permeability heterogeneous material (e.g., solidified monolithic, compacted granular fill, and backfilled grout). Eluent is introduced into a column of moderately-packed granular material in an up-flow pumping mode, with eluate collection performed as a function of the cumulative L/S. Up-flow pumping is considered to minimize air entrainment and flow channeling. The default eluent for most materials is reagent water; however, a solution of 1.0 mM calcium chloride in reagent water is used when testing materials with either a high clay content (i.e., to prevent deflocculation of clay layers) or high organic matter (i.e., to moderate mobilization of dissolved organic carbon). The flow rate is maintained between 0.5-1.0 mL/g L/S per day to increase the likelihood of local equilibrium between the solid and liquid phases, due to residence times longer than 1 day. Eluate volumes are chemically analyzed for a combination of inorganic and non-volatile organic analytes depending on the constituents of potential concern. Analyses of eluates for dissolved organic carbon and of the solid phase for total organic carbon afford evaluation of the impact of organic carbon release and the influence of dissolved organic carbon on the liquid-solid partitioning of inorganic constituents. For the purposes of chemical speciation modeling, the entire eluent volume up to 10 mL/g dry sample is collected in nine specific aliquots of varying volume. A limited subset of eluent volumes within the same L/S ratio range may be collected and analyzed for regulatory and compliance purposes. The column percolation test set-up is shown in Figure 2.
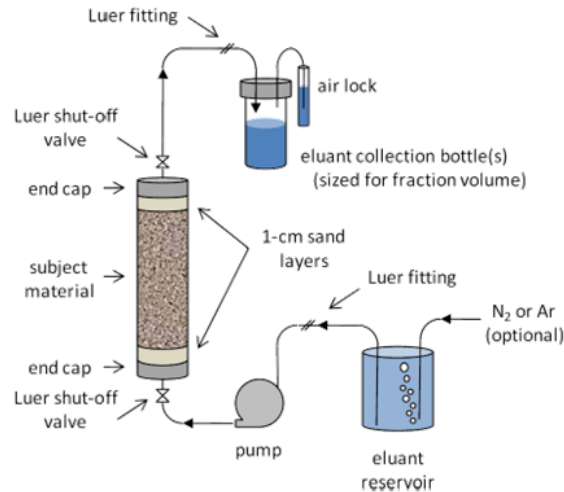
Figure 2. Column percolation test (Method 1314) [26].

DUAL REGIME PERCOLATION MODEL

A dual regime transport model coupled with chemical equilibrium calculations was used in this work for simulating flow through the size reduced grout material (representative of the cracked grout). The dual regime transport approach had also been acknowledged in the past for simulating flow through cracked concrete in grouted systems for radioactive waste disposal scenarios [1].

Several numerical models [27] such as equilibrium approach, dual permeability approach, and dual porosity approach were developed in the past to simulate flow of ionic species during infiltration through a heterogeneous structure with pores, cracks and fissures at various length scales as illustrated in Figure 3. The figure shows two different flow regimes – (1) advection controlled **mobile zone** incorporating solids with cracks and macropores, i.e. the fast pathway, and (2) the diffusion controlled **immobile zone** comprising of solid aggregates with micro/nano-scale pores i.e. the slow pathway. The idealization of Figure 3 is shown in Figure 4 where the aggregates comprising the diffusion controlled immobile regime are assumed to be spherical in shape to simplify model computations.
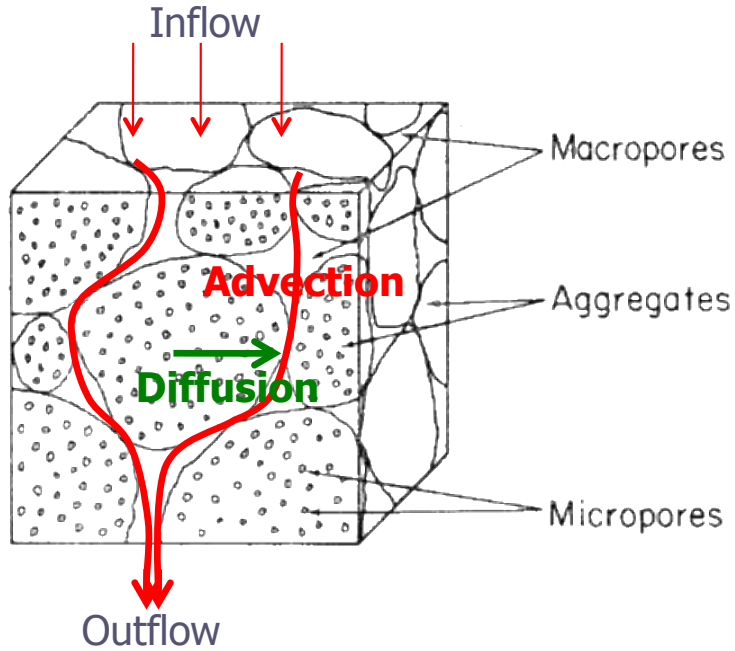
Figure 3. Preferential flow of ionic species through a heterogeneous structure (after [28]).
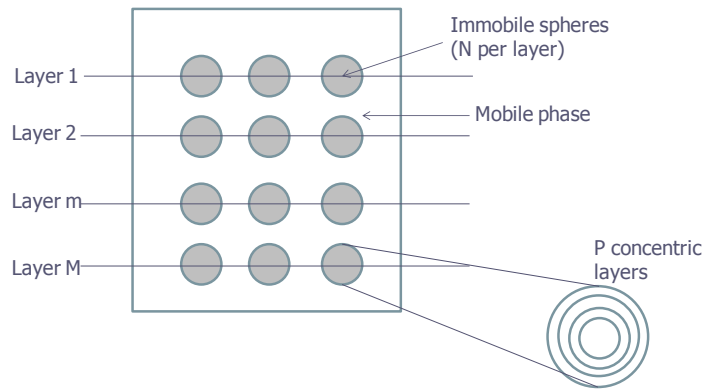

Figure 4. Idealization of heterogeneous system in advection-radial diffusion approach.

The governing equations for simulation of transport of species are given as [29]

$$\frac{\partial c_m}{\partial t} = \frac{\partial}{\partial x}(-q_m c_m) - Q \tag{1}$$

$$\frac{\partial c_{im}}{\partial t} = \frac{1}{r^2} D_{im} \frac{\partial}{\partial r}\left(r^2 \frac{\partial c_{im}}{\partial r}\right) \tag{2}$$

where c is the concentration of species in pore solution (moles/L), subscript m stands for mobile zone, subscript im stands for immobile zone, D_{im} $(= \frac{D^0}{\tau_{im}})$ is the diffusivity through the immobile zone (m²/s), τ_{im} is the tortuosity of the immobile zone, w stands for volume fraction of mobile zone, r is the radial dimension, R is the radius of the spherical aggregates (m), N is the number of aggregates in the system, V_0 is the volume of the system (m³), q_m is the volumetric water flux density of infiltrating water (m/s), Q is the mass exchange rate between mobile and immobile zones (moles/L/s), x is the spatial dimension (m) and t is time (s).

The dual regime transport model was implemented in the geochemical speciation code, ORCHESTRA, and coupled with chemical equilibrium calculations at each point in space and time to simulate the leaching of species through the cracked concrete. In the next section, the simulation results for the up-flow column percolation test are shown for the size reduced backfill grout material using the dual regime coupled reactive transport model and the model predictions are compared with the test data.

COMPARISON OF COLUMN PERCOLATION PREDICTIONS WITH TEST DATA

In the up-flow column percolation test, the backfill material was reduced to a particle size of 2 mm or less and filled a column of diameter 5 cm and length 30 cm. The flow rate through the column was adjusted to achieve a residence time of 0.9 L/S per day. The bed porosity was estimated to be 0.3 and the material porosity was estimated to be 0.21 for the monolithic material [7]. The aggregate radius in the immobile zone was assumed to be 2 mm. The model parameters that needed to be calibrated were tortuosity of the aggregates and volume fraction of the mobile zone. Using the leaching profiles of non-reactive ions such as potassium (K) and lithium (Li), the tortuosity and volume fraction were calibrated to be 400 and 15%, respectively. Initial pH of the material is estimated by balancing charge using H^+ and calculating initial equilibrium composition of the material using the selected mineral set. Figure 5 shows the comparisons of the model predictions for pH, ionic strength and leaching of major species with the column percolation test data. In the figure, the red circles and the green diamonds are the test data, blue squares are the average model predictions estimated at the time points corresponding to the test data from the blue line of continuous model predictions. It can be stated after evaluating the comparisons in the figure that the overall model predictions for the leaching of the major species, and specifically pH and ionic strength evolutions prove to be promising. However, the model predictions do not entirely reflect the trends in the leaching data requiring enhancement of the chemical description. Thus further research on refining the chemical characteristics of the material is warranted and will be continued.
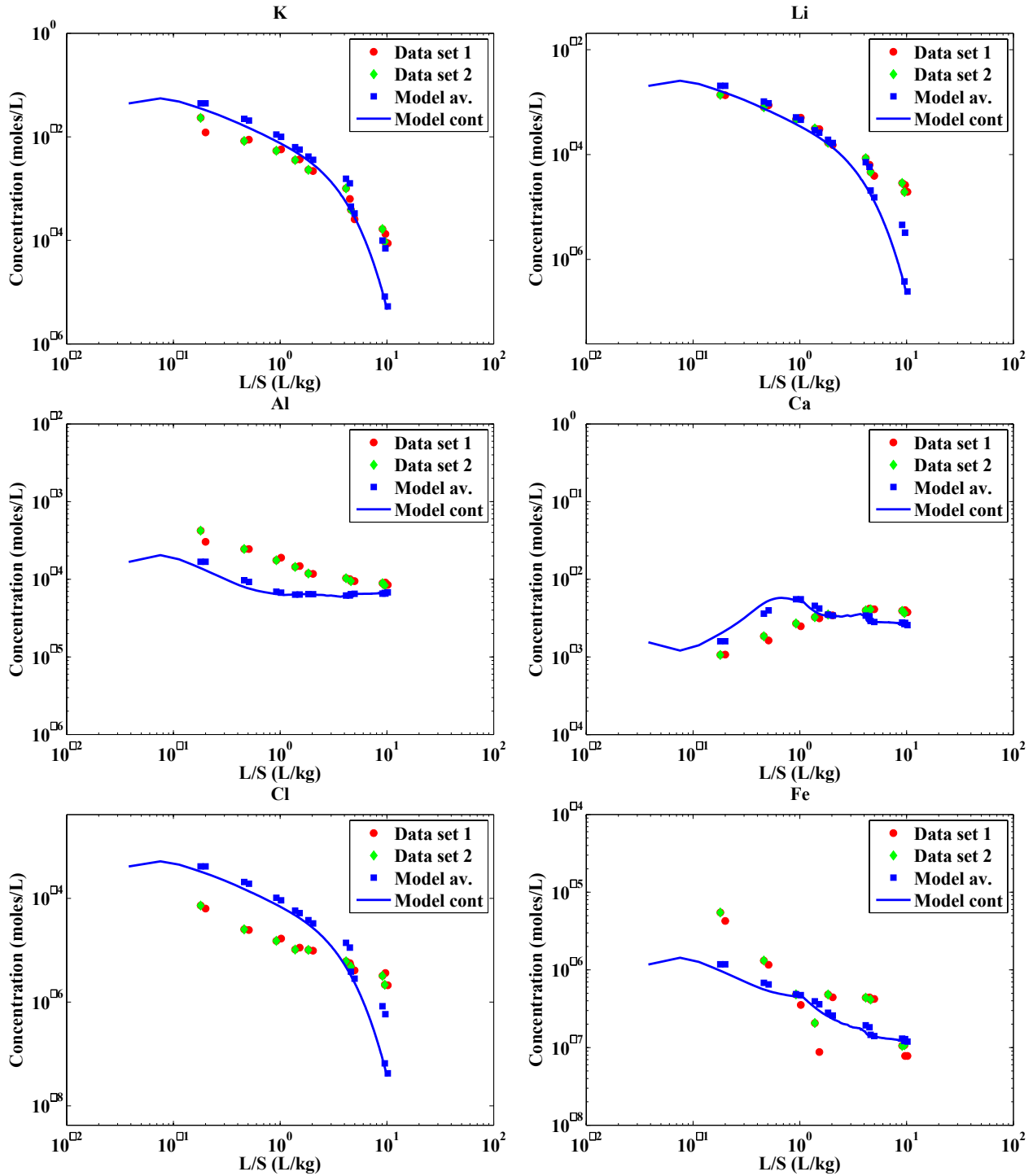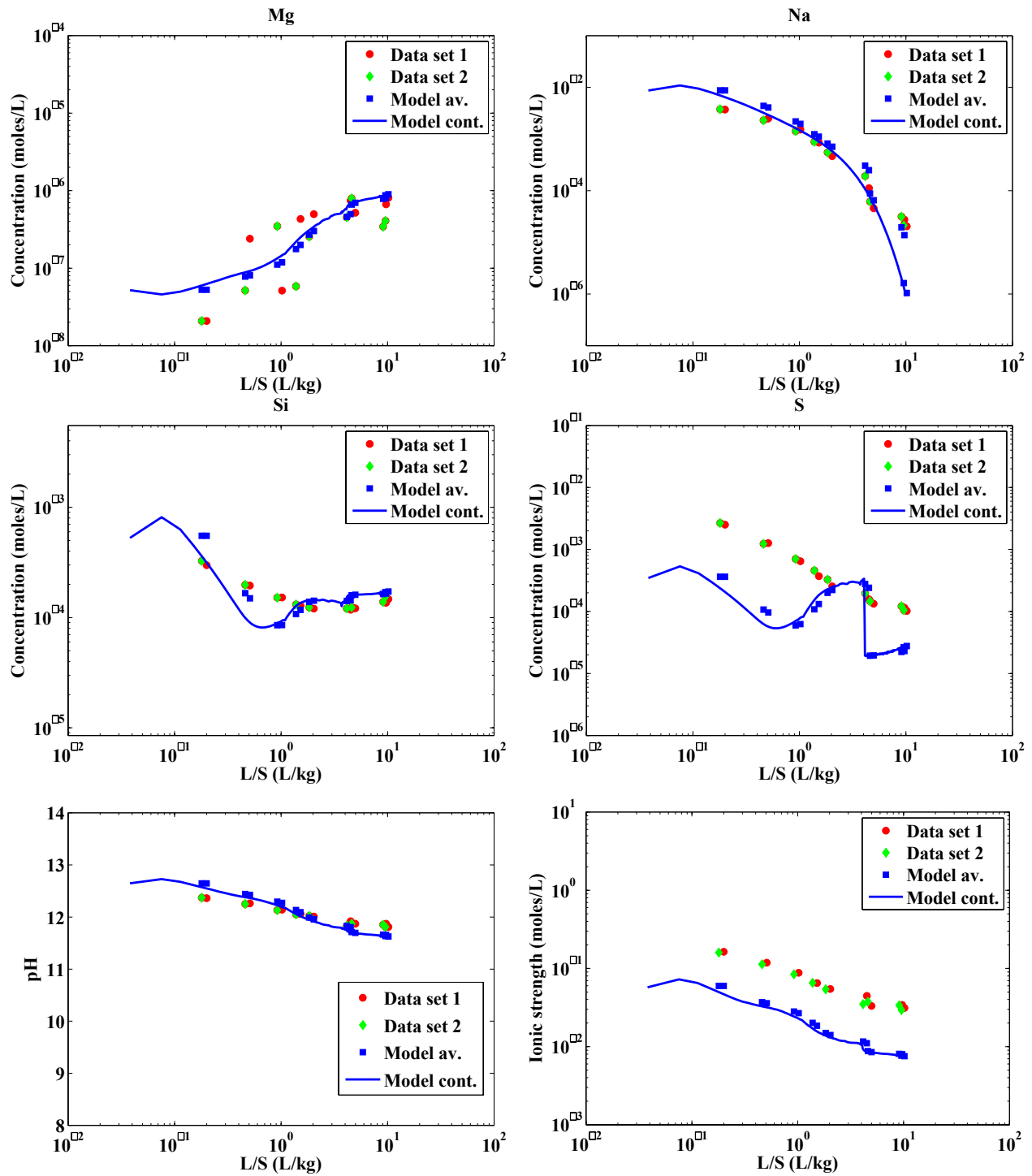
Figure 5. Comparison of model predictions with column percolation test data.

PREDICTION OF LEACHING THROUGH CRACKED CONCRETE

In this section, effects of crack state of the grout, infiltration rate, and simulation methodology are evaluated, on the pH evolution of the grout material (the master variable controlling release of the contaminants). The changes in physical and chemical characteristics of the material are expected to affect the release of the contaminants from the waste material. Thus it is important to understand the underlying behavior of the grout used for stabilization of the waste material. Ingress and reaction of atmospheric carbon dioxide is not considered here but can result in further decreases in pH (typically to pH ~9) than considered in this model; however carbon dioxide ingress also will be limited by significant resistance by cover materials to ingress. The impacts of carbon dioxide ingress will be the subject of future modeling cases.

A hypothetical test case[2] was set up for assessing pH evolution of the grout material at the interface of the grout and the residual waste (assumed to be residing at the bottom of the tank [30]). The depth of the tanks at Hanford site varies between 9 and 16 m [31]. In the simulation the tank was assumed to be 9 m deep. Full-scale grout test pour conducted at INL tank farm facility indicated that cracks were visible at a spacing of 1 m [1]. However, hardened grout in place at INL tank farm did not show any visible surface cracks [1]. The aggregate diameter in the dual regime model was assumed to be 1 m. For the base case, the following parameters were assumed - infiltration rate: 377 mm/year (same as that at Savannah River Site [2]), total porosity: 0.25, mobile volume fraction (fast pathway): 15%. In order to assess the effects of crack state of the structure, the pH evolutions were evaluated for mobile volume fractions of 10, 15, and 20% (low to moderate cracking) while keeping the other parameters at the base case values. Using the base case parameter values, it was estimated to take approximately 1800 years to reach L/S ratio of 10 (the same as the final target L/S in the up-flow column percolation tests). Thus for comparison purposes, all the simulations were performed for 1800 years in this section. Figure 6 shows the effects of mobile volume fraction (crack state) on the pH evolution with time. It can be observed from the figure that if the mobile volume fraction is more, it takes more time to lower pH, which is counter-intuitive, but occurs because the percolating water is in local equilibrium with a larger fraction of the grout. In the cases assessed in this section, the total grout porosity was assumed to be constant and the mobile zone porosity was accordingly adjusted. If the mobile volume fraction is less, the mobile zone porosity becomes more to achieve the same total porosity (see Eq. (3)). Hence the volume of infiltrated water in contact with the immobile zone becomes more, leading to a faster decrease in pH.

$$\varphi_t = w\varphi_m + (1 - w)\varphi_{im} \tag{3}$$

where φ_t is the total porosity of the structure.

---

[2] This test case was set up to illustrate the approach, but is not intended to simulate the specific test conditions of high level waste tank closure at any specific site.
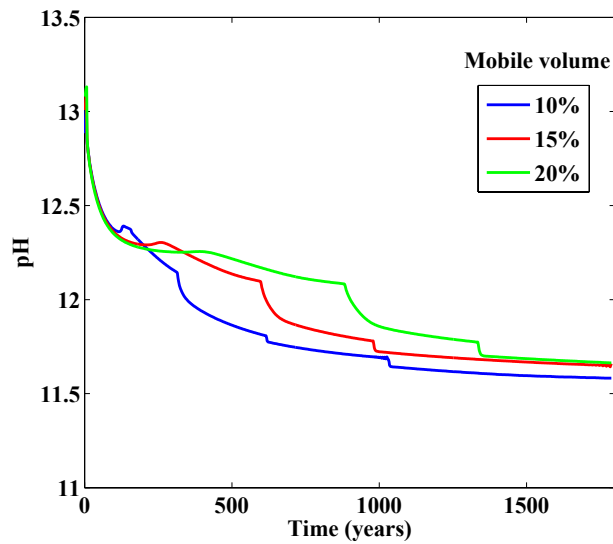
Figure 6. Effects of mobile volume fraction on pH evolution at grout-waste interface.

Infiltration rate through the tank grout depends on various factors such as climatic conditions, soil type, and vegetation over the ground. It varies from 377 mm/year at the Savannah River Site [2] to 0-100 mm/year at Hanford Tank Farm area [32]. In order to assess the effects of infiltration rate on leaching, the infiltration rate was varied at 377, 300, 200, 100 and 10 mm/year while keeping the other parameters at the base case values (mobile volume fraction: 15%, total porosity: 0.25). The pH evolutions for the above-mentioned cases are shown in Figure 7. As expected, the figure shows that the pH evolution rate decreases with decrease in the infiltration rate. It is also evident from the figure that the pH evolution rate is significantly different for infiltration of 10 mm/year from the rest. The slow infiltration rate results in more contact time between the infiltrating water (mobile zone) and the solid matrix (immobile zone) leading towards equilibrium between the zones. Thus the pH evolution for slow infiltration rate has more contribution from the immobile zone than the faster infiltration rates.
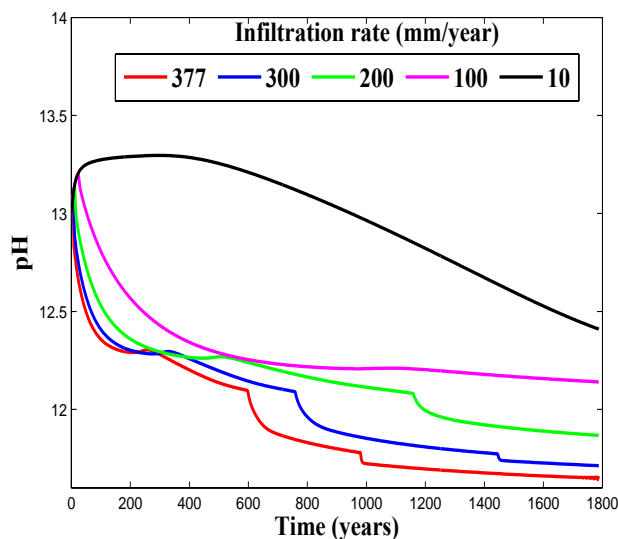
Figure 7. Effects of infiltration rate on pH evolution at grout-waste interface.

It can be observed from figures 6 and 7 that the pH evolution is related to the physical characteristics of the material (crack state), and the boundary conditions of the structure (infiltration rate). Moreover, the pH evolution is also dependent on the chemical composition of the material as was observed in Denham (2007) [30]. It was shown that the pH changes in the pore solution of the tank grout due to infiltration of rainwater were dependent on the mineral phases allowed to form in the simulation. It is important to note that the grout composition and the mineral set considered in Denham (2007) are different from those used in this paper. The mineral set used in this study is selected using controlled and standardized leaching test data mentioned earlier. In Denham (2007), equilibrium compositions were calculated after an equivalent pore volume with rainwater composition (Table 3) entered the structure, and then the pore water was flushed out and a fresh pore volume with the same rainwater composition entered the structure (known as "Flush" mode).

Following the above "flush" mode approach for the hypothetical test case evaluated here, the pH evolution at the grout-waste interface as a function of number of pore volume was evaluated using rainwater composition at the Savannah River site [30] flowing through the grout. In these simulations, one pore volume having the composition of rainwater was brought in contact with the solid. Then, after calculating the equilibrium composition, a fresh volume of pore water was brought in contact with the solid. This process was repeated for 120 pore volumes (the number of pore volumes passed in 1800 years). The number of pore volumes passed through the structure was then converted to time (years) using the infiltration rate at SRS (377 mm/year), total porosity of 0.25, and tank depth of 9 m. The dual regime (base case) and flush mode simulation results are compared in Figure 8. The figure shows sudden drops in pH for the case of flush mode simulation whereas the dual regime model shows a more realistic and smoother pH evolution. This is a significant advantage of using the coupled dual regime reactive transport model for

15

evaluating time dependent chemical changes as a result of infiltration flowing through cracked grout.

Table 3. Chemical composition of rain water at SRS after [30].

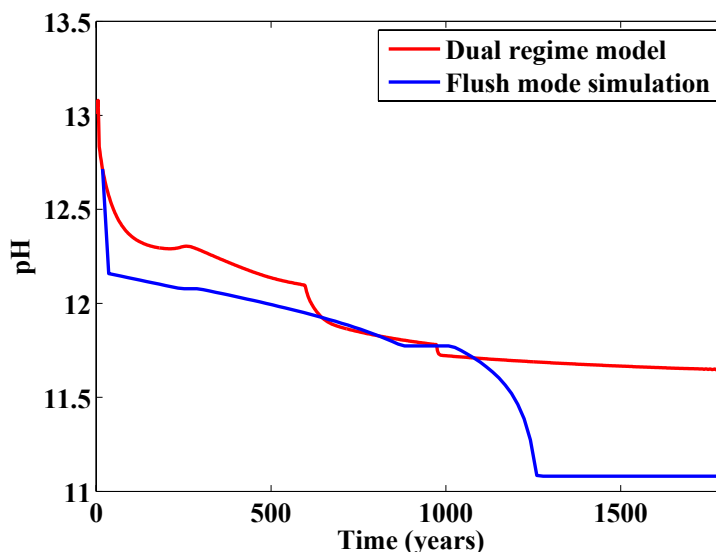| Constituents	Concentrations Moles/L
O_2	2.5×10^{-4}
CO_2	1.1×10^{-5}
SO_4^{-2}	1.3×10^{-5}
Cl^-	9.9×10^{-6}
Na^+	8.7×10^{-6}
Ca^{+2}	2.1×10^{-6}
Mg^{+2}	1.3×10^{-6}

Figure 8. pH evolution as a function of time using dual regime model and flush mode simulation.

It is important to acknowledge that while predicting chemical evolutions at the grout-waste interface, chemical composition, physical condition, and boundary conditions should be considered with equal emphasis and synergistically with controlled test data. Hence, a flexible and robust numerical simulation framework as presented in this paper proves to be promising and useful in estimating potential release rate of constituents such as radionuclides from the high-level tank wastes after closure.

It is also important to consider uncertainty in various physical and chemical characteristics, and boundary conditions (e.g., carbonation) while assessing long-term release of constituents from the tank after closure. Uncertainty in the input parameters (e.g., physical characteristics

such as porosity and initial concentrations of constituents, and boundary conditions) can be quantified using multiple sets of input parameter measurements. The model parameters (e.g., tortuosity and mobile volume fraction) can also be calibrated using multiple sets of test data. Finally, the uncertainty in the model predictions can be evaluated by propagating the input and model parameter uncertainties using techniques available in the literature such as Monte Carlo simulation [33]. The uncertainty quantification and propagation techniques can be used with the dual regime reactive transport model for assessing uncertainty in the leaching predictions. Thus the simulation framework presented in this paper can be used in evaluating the effectiveness of the current grout materials and future grout designs while considering various sources of system and environmental uncertainty.

SUMMARY

A numerical simulation framework is presented in this paper for simulating pH evolutions and release of major species from the cracked cementitious grout used for stabilization of the high-level wastes. The dual regime reactive transport model implemented for numerical simulation of release of constituents due to infiltration through cracked grout takes into account advection through the mobile zones comprising of solid materials containing cracks and macropores, and immobile zones comprising of micropores and most of the cement matrix. The mineral composition of the grout material was selected by comparing leaching predictions using various mineral sets with the leaching test data as a function pH for the grout material. The dual regime coupled reactive transport model predictions were then compared with the up-flow column percolation test data for the size-reduced grout. Finally, the effects of the crack state of the grout, infiltration rate, and simulation method on the pH evolutions (the master variable affecting release of contaminants) at the grout-waste interface were evaluated. The simulation framework is flexible enough to incorporate various physical and chemical characteristics of grout compositions, and the robust tiered approach of selection of mineral phases, calibration of model parameters, and finally simulation of the cracked grout is built upon controlled and reproducible test data. Thus the coupled reactive transport model developed in this work proves to be promising for assessing potential risks from leaching of a cracked grout in a closed tank containing constituents of human health and environmental concern.

REFERENCES

1. Pabalan, R. T., Glasser, F. P., Pickett, D. A., Walter, G. R., Biswas, S., Juckett, M. R., Sabido, L. M., and Myers, J. L., Review of literature and assessment of factors relevant to performance of grouted systems for radioactive waste disposal, Center of Nuclear Waste Regulatory Analyses San Antonio, TX 78228-0510, 2009.
2. Performance assessment for the H-area tank farm at the Savannah River Site, Savannah River Remediation LLC, Closure and Waste Disposal Authority, 2011.
3. Retrieval Performance Evaluation Methodology for the AX Tank Farm, U.S. Department of Energy, Richland Operations Office, 1999.
4. Riley, R. G., and Lopresti, C. A., Data catalog for models simulating release of contaminants from Hanford Site Waste Sources, Pacific Northwest National Laboratory, 2001.
5. Wan, J., Larsen, J. T., Tokunaga, T. K., and Zheng, Z., pH Neutralization and Zonation in Alkaline-Saline Tank Waste Plumes, Environmental Science & Technology, 38(5), 2004, pp. 1321-1329.
6. Draft Tank Closure and Waste Management Environmental Impact Statement for the Hanford Site, Richland, Washington, U.S. Department of Energy, 2009.
7. Langton, C., Kosson, D., and Garrabrants, A., REFERENCE CASES FOR USE IN THE CEMENTITOUS PARTNERSHIP PROJECT, 2010.
8. Garrabrants, A. C., Kosson, D. S., Van der Sloot, H., Sanchez, F., and Hjelmar, O., Background information for the Leaching Environmental Assessment Framework (LEAF) test methods (EPA/600/R-10/170), EPA, 2010.
9. Garrabrants, A. C., Kosson, D. S., Stefanski, L., Delapp, R., Seignette, P. F. A. B., Van der Sloot, H. A., Kariher, P., and Baldwin, M., Interlaboratory validation of the leaching assessment framework (LEAF) Method 1313 and Method 1316, U.S. EPA Office of Research and Development, Air Pollution Control Division, 2012.
10. U.S. Environmental Protection Agency, Wastes - hazardous waste - test methods; New test methods on-line.
11. Cementitious Barriers Partnership.
12. van der Sloot, H., van Zomeren, A., Stenger, R., Schneider, M., Spanka, G., Stoltenberg-Hansson, E., and Dath, P., Environmental CRIteria for CEMent-based products (ECRICEM) Phase I: Ordinary Portland cements and Phase II: Blended cements, executive summary, ECV-E-11-020, Netherlands Energy Research Foundation, 2008.
13. van der Sloot, H., Seignette, P., Comans, R. N. J., van Zomeren, A., Meeussen, J. C. L., Kosson, D. S., and Hjelmar, O., Evaluation of environmental aspects of alternative materials using an inetgrated approach assisted by a database/expert system, International Symposium on Recycling and Reuse of Materials, University of Dundee, Dundee, Scotland, 2003, .
14. van der Sloot, H., Hoede, D., Rietra, R. P. J. J., Stenger, R., Lang, T., Schneider, M., Spanka, G., Stoltenberg-Hansson, E., and Lerat, A., Environmental criteria for cement-based products, ECRICEM I, ECN C-01-069, Netherlands Energy Research Foundation, 2001.
15. Meeussen, J. C. L., ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models, Environmental Science and Technology, 37(6), 2003, pp. 1175-1182.
16. Allison, J. D., Brown, D. S., and Novo-gradac, K. J., MINTEQA2, geochemical assessment model for environmental systems, version 3., U.S. Environmental Protection Agency, 1992.

17. Lothenbach, B., Matschei, T., Möschner, G., and Glasser, F. P., Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement, Cement and Concrete Research, 38(1), 2008, pp. 1-18.

18. Samson, E., Lemaire, G., Marchand, J., and Beaudoin, J. J., Modeling chemical activity effects in strong ionic solutions, Computational Materials Science, 15, 1999, pp. 285-294.

19. Dmitrii A. Kulik, M. K., Aqueous Solubility Diagrams for Cementitious Waste Stabilization Systems: II, End-Member Stoichiometries of Ideal Calcium Silicate Hydrate Solid Solutions, Journal of the American Ceramic Society, 84(12), 2001, pp. 3017-3026.

20. Lothenbach, B., and Winnefeld, F., Thermodynamic modelling of the hydration of Portland cement, Cement and Concrete Research, 36(2), 2006, pp. 209-226.

21. Samson, E., and Marchand, J., Modeling the transport of ions in unsaturated cement-based materials, Computers & Structures, 85(23-24), 2007, pp. 1740-1756.

22. Zevenbergen, C., Reeuwijk, L. P. van, Bradley, J. P., Bloemen, P., and Comans, R. N. J., Mechanism and conditions of clay formation during natural weathering of MSWI bottom ash, Clays and Clay Minerals, 44(4), 1996, pp. 546-552.

23. Sugiyama, D., and Fujita, T., A thermodynamic model of dissolution and precipitation of calcium silicate hydrates, Cement and Concrete Research, 36(2), 2006, pp. 227-237.

24. Zhang, T., Cheeseman, C. R., and Vandeperre, L. J., Development of low pH cement systems forming magnesium silicate hydrate (M-S-H), Cement and Concrete Research, 41(4), 2011, pp. 439-442.

25. Garrabrants, A. C., Kosson, D. S., Delapp, R., Kariher, P., Seignette, P. F. A. B., Van der Sloot, H. A., Stefanski, L., and Baldwin, M., Interlaboratory validation of the leaching environment assessment framework (LEAF) Method 1314 and Method 1315, U.S. EPA Office of Research and Development, Air Pollution Control Division, 2012.

26. Liquid-solid partitioning as a function of liquid-solid ratio for constituents in solid materials using an up-flow percolation column procedure, http://www.vanderbilt.edu/leaching/downloads/test-methods/, 2009.

27. Simunek, J., Jarvis, N. J., van Genuchten, M. T., and Gärdenäs, A., Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone, Journal of Hydrology, 272(1-4), 2003, pp. 14-35.

28. Gerke, H. H., and van Genuchten, M. T., A dual-porosity model for simulating the preferential movement of water and solutes in structures porous media, Water Resources Research, 29(2), 1993, pp. 305-319.

29. van Beinum, W., Meeussen, J. C. L., Edwards, A. C., and van Riemsdijk, W. H., Transport of ions in physically heterogeneous systems; convection and diffusion in a column filled with alginate gel beads, predicted by a two-region model, Water Research, 34(7), 2000, pp. 2043-2050.

30. Denham, M., Conceptual model of waste release from the contaminated zone of closed radioactive waste tanks, Washington Savannah River Company, 2007.

31. Sites, C. on the M. of C. R. W. S. S. in T. at T. D. of E., and Council, N. R., Tank Waste Retrieval, Processing, and On-site Disposal at Three Department of Energy Sites: Final Report, National Academies Press, 2006, .

32. Duncan, J. P., Burk, K. W., Chamness, M. A., Fowler, R. A., Fritz, B. G., Hendrickson, P. L., Kennedy, E. P., Last, G. V., Poston, T. M., and Sackschewsky, M. R., Hanford Site National Environmental Policy Act (NEPA) Characterization, Pacific Northwest National Laboratory (PNNL), Richland, WA (US), 2007.

33. Haldar, A., and Mahadevan, S., Probability, Reliability, and Statistical Methods in Engineering Design, John Wiley and Sons, 2000.