

ICEM03-4509

**VITRIFIED WASTE CORROSION RATES FROM FIELD EXPERIMENT AND REACTIVE
TRANSPORT MODELING**

**Diana H. Bacon/Pacific Northwest
National Laboratory**

Michael I. Ojovan/The University of Sheffield

**B. Peter McGrail/Pacific Northwest
National Laboratory**

**Natalie V. Ojovan/Scientific and
Industrial Association "Radon"**

**Irene V. Startseva/Scientific and
Industrial Association "Radon"**

ABSTRACT

The Hanford Site in southeastern Washington State has been used extensively by the U.S. Department of Energy (DOE) to produce nuclear materials for the U.S. strategic defense arsenal. A large inventory of radioactive and mixed waste has accumulated in 177 buried single- and double-shell tanks. Liquid waste recovered from the tanks will be pre-treated to separate the low activity fraction from the high-level and transuranic wastes. The low-activity waste (LAW) will be immobilized in glass and placed in a near-surface disposal system on the Hanford Site. Vitrifying the LAW will generate over 160,000 m³ of glass. Before the immobilized low-activity waste (ILAW) can be disposed, DOE must approve a performance assessment (PA), which is a document that describes the long-term impacts of the disposal facility on public health and environmental resources. A sound scientific basis for determining the long-term release rates of radionuclides from LAW glasses must be developed if the PA is to be accepted by regulators and stakeholders. To conduct this calculation, Pacific Northwest National Laboratory (PNNL) used a methodology in which the waste form release rate was calculated by modeling the basic physical and chemical processes that are known to control dissolution behavior using a reactive transport code, STORM [1]. This methodology was used instead of empirical extrapolations from laboratory "leaching" experiments commonly used in other PA or in the phenomenological approach of SIA "Radon" [2]. This methodology is preferred because the dissolution rate, and hence radionuclide release rate, from silicate glasses is not a static variable — a constant that can be derived independently of other variables in the system. Glass dissolution rate is a function of three variables (neglecting glass composition itself):

temperature, pH, and composition of the fluid contacting the glass. SIA Radon has been running a field experiment for over 12 years to evaluate the behavior of a high sodium glass buried in a loamy soil. The radioactive waste glass (K-26) made from actual intermediate-level waste from the Kursk (RBMK) reactor was manufactured and placed in a shallow trench. The waste stream was 86 mass% NaNO₃, very similar to the salt content expected for Hanford LAW. The final glass composition had a Na₂O content of roughly 16 mass%, making it very relevant to the glass formulations being considered at Hanford. A joint US DOE-SIA Radon project was devised to validate the modeling approach used for the ILAW PA by modeling glass corrosion in the subsurface experimental facility [3]. This paper gives an estimate of glass corrosion and ion exchange rates for K-26 waste glass based on field measurements.

INTRODUCTION

SIA Radon Field Experiment

SIA Radon has been running a field experiment for over 12 years to evaluate the behavior of a high sodium glass buried in a loamy soil. The radioactive waste glass (K-26) made from actual intermediate-level waste from the Kursk (RBMK) reactor was manufactured and placed in a shallow trench. The waste stream was 86 mass% NaNO₃, very similar to the salt content expected for Hanford LAW. The final glass composition had a Na₂O content of roughly 16 masspercentage, making it very relevant to the glass formulations being considered at Hanford. In FY01, the SIA Radon researchers

responsible for the 14-year-old *in-situ* testing were contacted to pursue possible joint SIA Radon-U.S. DOE study of their test samples and results.

A key International Atomic Energy Agency (IAEA) deliverable describing the test program and current results was issued [1]. This report describes the *in-situ* testing program in which borosilicate, cement, and bitumen waste forms were placed in a configuration open to the elements site and in a shallow-subsurface repository. The corrosion behaviour of the waste forms was evaluated by monitoring the waste component concentrations (primarily ^{137}Cs) in contacting water. After 12 years of testing, the burial site was opened for visual examination, sampling and analysis. The glass composition, physical appearance of the glass after testing, concentrations of key glass components in leachate solutions (as a function of time), and corrosion rate models were studied [2].

Hanford Site

The Hanford Site in southeastern Washington State has been used extensively by the U.S. Department of Energy (DOE) to produce nuclear materials for the U.S. strategic defense arsenal. A large inventory of radioactive and mixed waste has accumulated in 177 buried single- and double-shell tanks. Liquid waste recovered from the tanks will be pretreated to separate the low-activity fraction from the high-level and transuranic wastes. The low-activity waste (LAW) will be immobilized in glass and placed in a near-surface disposal system on the Hanford Site. Vitrifying the LAW will generate over 160,000 m³ of glass. The volume of immobilized low-activity waste (ILAW) at Hanford is among the largest within the DOE complex and comprises one of the largest inventories of long-lived radionuclides planned for disposal in a low-level waste facility (approximately 2.4 million curies total activity). Before the ILAW can be disposed, DOE must approve a performance assessment (PA), which is a document that describes the long-term impacts of the disposal facility on public health and environmental resources. A sound scientific basis for determining the long-term release rates of radionuclides from LAW glasses must be developed if the PA is to be accepted by regulators and stakeholders.

The 1998 version of the ILAW PA [3] showed that a key variable in the analysis is the waste form release rate, which must be calculated over a period of thousands of years. To conduct this calculation, we used a methodology in which the waste form release rate was evaluated by modeling the basic physical and chemical processes that are known to control dissolution behavior instead of using empirical extrapolations from laboratory "leaching" experiments commonly used in other PAs. We adopted this methodology because the dissolution rate, and hence radionuclide release rate, from silicate glasses is not a static variable — a constant that can be derived independently of other variables in the system. Glass dissolution rate is a function of three variables (neglecting glass composition itself): temperature, pH, and composition of the fluid contacting the glass [4].

The temperature of the ILAW disposal system is a known constant. However, both the pH and the composition of the fluid contacting the glass are variables that are affected by flow rate, reactions with other engineered materials, gas-water equilibria, secondary phase precipitation, alkali ion exchange, and dissolution of the glass itself (a classic feedback mechanism). Consequently, glass dissolution rates will vary both in time and as a function of position in the disposal system. There is no physical constant such as a "leach rate" or radionuclide release rate parameter that can be assigned to a glass waste form in such a dynamic system.

The computer code selection criteria and selection process used are documented in *Selection of a Computer Code for Hanford Low-Level Waste Engineered-System Performance Assessment* [5]. The needed capabilities were identified from an analysis of the important physical and chemical processes expected to affect LAW glass corrosion and the mobility of radionuclides. The available computer codes with suitable capabilities were ranked in terms of the feature sets implemented in the code that match a set of physical, chemical, numerical, and functional capabilities needed to assess release rates from the engineered system. The highest-ranked computer code was found to be the STORM code developed at Pacific Northwest National Laboratory (PNNL) for evaluating arid land disposal sites. The verification studies for STORM are documented in *Subsurface Transport over Reactive Multiphases (STORM): A General, Coupled Nonisothermal Multiphase Flow, Reactive Transport, and Porous Medium Alteration Simulator, Version 2, User's Guide* [6].

Joint Research Project

The intention of the joint U.S. DOE - SIA Radon research project is to use the data and samples generated during the Russian *in-situ* testing program as validation for the Hanford site PA source term testing and modeling approach. The approach taken in this joint program is to generate the data inputs for STORM modeling from existing and new data on the Russian glass, burial facility, and environmental parameters. Predicted release will be compared to measured values and the model will be updated based on the results.

This paper presents results of STORM modeling, using estimates of waste glass dissolution rates based on laboratory measurements of Hanford waste glasses.

FIELD DATA

Effluent collected from a catch basin containing a sample of sodium waste glass named K-26 shows generally decreasing B (Fig. 1) and Cl (Fig. 2) and increasing Na⁺ (Fig. 3) with time, relative to consistent control values. Effluent pH (Fig. 4) varies with time, but K-26 leachate is approximately 1 pH unit higher than control values. Water flow rate through the catch basin (Fig. 5) was estimated by dividing the volume of water collected and dividing by the sampling interval. The steady-

state recharge rate was estimated for the site based on volumes of water samples collected over time from the pan containing the waste glass. To obtain the recharge rate, the water volume

was divided by the surface area of the collection pan and the time elapsed since the last sample collected. These recharge rates were averaged to estimate a steady state recharge rate of 38.5 cm/yr.

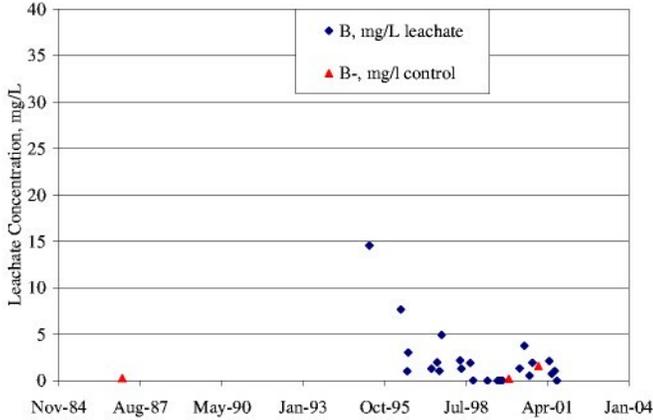


Fig. 1. Measured boron content from K-26 waste glass experiment at SIA RADON field site.

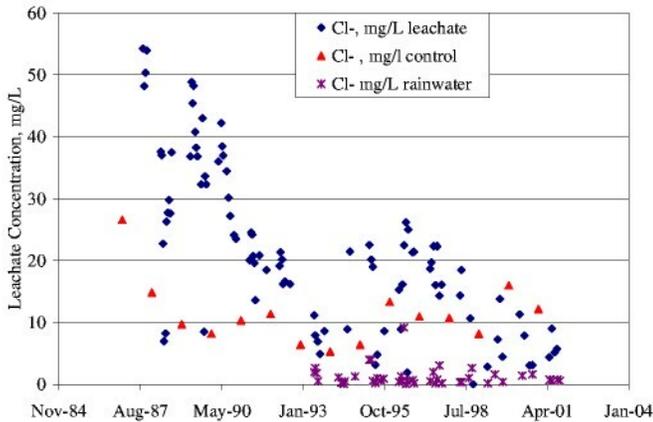


Fig. 2. Measured chloride content from K-26 waste glass experiment at SIA RADON field site.

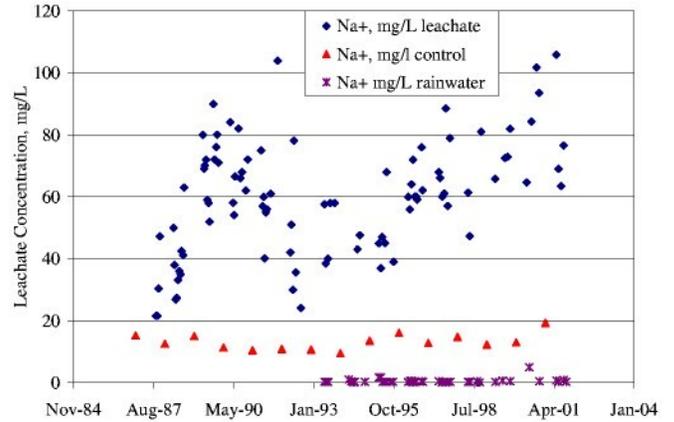


Fig. 3. Measured sodium content from K-26 waste glass experiment at SIA RADON field site.

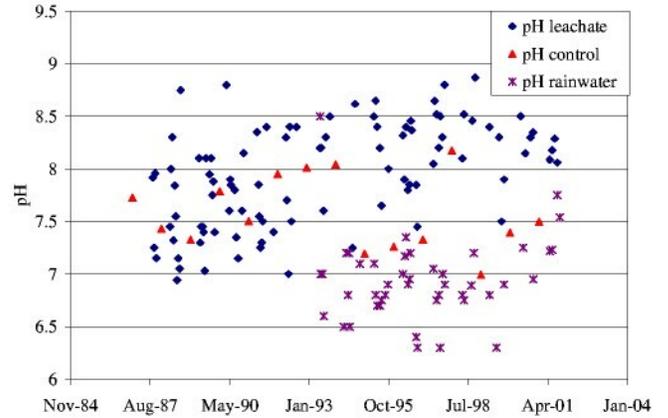


Fig. 4. Measured pH from K-26 waste glass experiment at SIA RADON field site.

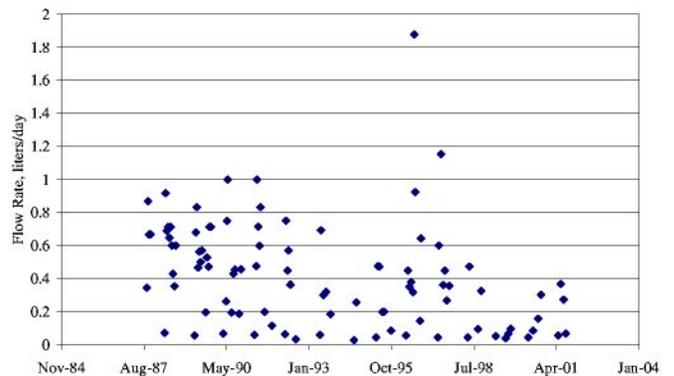


Fig. 5. Flow rate of leachate from K-26 waste glass experiment at SIA RADON field site.

MODELING

The model is based on an experimental shallow-ground repository for K-26 waste glass (Fig. 6). Four materials are present in the area to be modeled: backfill soil, coarse sand filler, waste glass, and a carbon steel container.

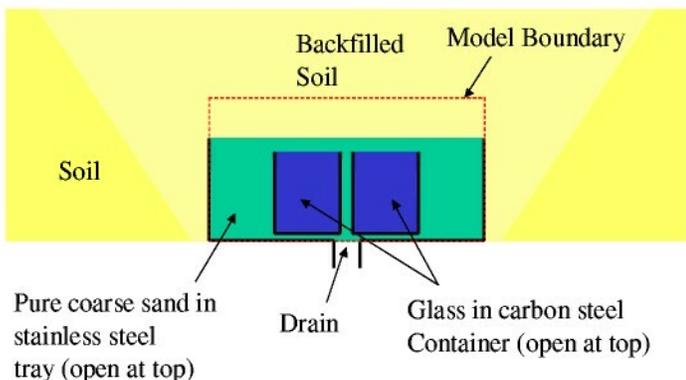


Fig. 6. Layout of SIA RADON Field Experiment

Unsaturated hydraulic properties for the backfill soil and coarse sand surrounding the waste glass were estimated from particle size data provided by SIA RADON (Table I). The estimation methods used combine theory with empirical fitting parameters [7-9]. Unsaturated hydraulic properties for the waste glass were assumed to be the same as used previously the ILAW waste glasses, with the exception of higher residual water content. The steel container was assumed have the same hydraulic properties as the glass.

Table I. Unsaturated hydraulic properties for SIA RADON Field Experiment

	Particle Density (g cm ⁻³)	Porosity	Saturated Hydraulic Conductivity (cm s ⁻¹)	van Genuchten α (cm ⁻¹)	van Genuchten n	Residual Saturation
Backfill Soil	3.00	0.22	6.37x10 ⁻⁶	1.39x10 ⁻²	1.32	1.00x10 ⁻⁴
Coarse Sand	2.23	0.27	3.33x10 ⁻³	2.37x10 ⁻¹	4.89	3.26x10 ⁻²
Waste Glass	2.68	0.02	1.00x10 ⁻²	2.00x10 ⁻¹	3.00	2.30x10 ⁻²

Using the estimated recharge rate of 38.5 cm/yr, a flow simulation was run to steady state using the STOMP [10] code (Fig. 7), which is the flow part of STORM. Water flows in uniformly across the entire upper boundary. Flow out of the system is limited to a 7-cm wide drain in the center of the lower boundary. The water saturation in the backfill soil is close to 20% at a recharge rate of 38.5 cm/yr. The backfill soil has a greater percentage of fines than the sand filler, which is 98%

sand, so the sand filler drains more easily and has a water content of 9% at this recharge rate. The waste glass drains the most easily because it is fractured and has no matrix porosity, so it has the lowest water content of 0.7%.

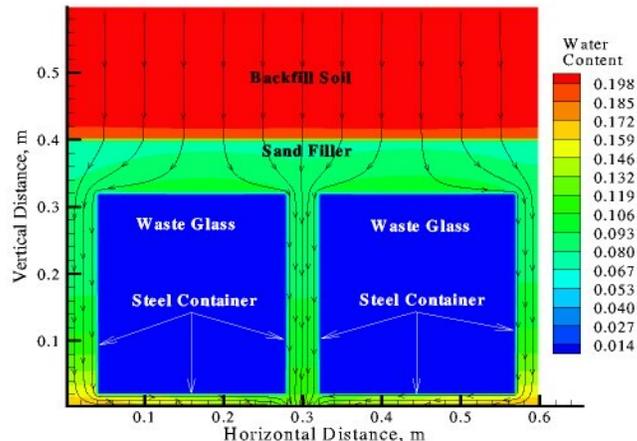


Fig. 7. Steady state flow field for SIA RADON Field Experiment

The waste glass blocks were contained in carbon steel DD3 (Russian standard, reference book data). The composition of the carbon steel container was assumed to be: 99% Fe, 0.14% C, 0.4% Mn, 0.04% P, 0.3% S, and 0.12% Si. The corrosion rate was reported to be 0.5 g/m²/d.

The composition of the backfill soil and sand was determined (Table II). A few minor constituents, vermiculite, hornblende and hydromica, were not listed in the EQ3/6 database. The waste glass composition and composition of shallow groundwater were used to develop EQ3/6 simulations. The results of these simulations were used to identify likely aqueous (Table IV) and secondary mineral species (Table V) resulting from the dissolution of K-26 waste glass in shallow groundwater. These phase assemblages will be updated with actual phases observed once examination of reacted glass samples has been completed by SIA RADON.

Table II. Mineral composition of Backfill Soil and Sand Filler used in SIA RADON Field Experiment

	Soil	Sand
Quartz	76.9%	81.3%
Microcline	10.8%	4.6%
Albite	4.9%	7.6%
Illite	2.7%	1.5%
Smectite	2.6%	1.2%
Calcite	1.2%	1.8%
Dolomite	0.8%	2.1%

Table III. SIA RADON K-26Waste Glass Composition

Oxide	Wt%	Oxide	Wt%
Al ₂ O ₃	2.5%	SiO ₂	48.2%
B ₂ O ₃	7.5%	MnO	0.95%
CaO	15.5%	PbO	0.95%
NaCl	1.2%	TiO ₂	0.95%
Fe ₂ O ₃	1.7%	MoO ₃	0.95%
K ₂ O	0.5%	SnO ₂	0.95%
Na ₂ O	16.1%	P ₂ O ₅	0.95%
Na ₂ SO ₄	1.1%		

Table V. Secondary mineral species identified by EQ3/6 simulations of K-26 waste glass dissolution in groundwater

Mineral Name	Formula
Calcite	CaCO ₃
Cassiterite	SnO ₂
Celadonite	KMgAlSi ₄ O ₁₀ (OH) ₂
Cerussite	PbCO ₃
Chalcedony	SiO ₂
Diaspore	AlHO ₂
Dolomite-ord	CaMg(CO ₃) ₂
Hematite	Fe ₂ O ₃
Nontronite-Ca	Ca _{1.165} Fe ₂ Al _{1.33} Si _{3.67} H ₂ O ₁₂
Nontronite-Na	Na _{1.33} Fe ₂ Al _{1.33} Si _{3.67} H ₂ O ₁₂
Pyrolusite	MnO ₂
Pyromorphite	Pb ₅ (PO ₄) ₃ Cl
Anatase	TiO ₂
Stilbite	Ca _{1.019} Na _{1.136} K _{0.006} A _{12.18} Si _{6.82} O ₁₈ ·7.33H ₂ O

For a dissolution reaction involving glass, parameters associated with the following kinetic rate law are needed:

$$r_g = \bar{k} \alpha_{H^+}^{-\eta} e^{-\frac{E_a}{RT}} \left[1 - \left(\frac{Q}{K_g} \right) \right] \quad (2)$$

where: r_g = dissolution rate, g m⁻² d⁻¹, \bar{k} = intrinsic rate constant, g m⁻² d⁻¹, α_{H^+} = hydrogen ion activity (variable to be calculated by STORM), E_a = activation energy, kJ/mol, R= gas constant, kJ/(mol·K), T = temperature, degrees K (assumed constant at 15°C), Q = ion activity product Glass (variable to be calculated by STORM), K_g = pseudoequilibrium constant, η = pH power law coefficient.

Initially, glass dissolution rate parameters for the K-26 glass (Table VI) were assumed to be similar to the laboratory-measured values for LAWABP1 and HLP-31 glass [4], and adjusted to fit observed data.

Table VI. Rate parameters assumed for K-26 glass dissolution

Parameter	Meaning	Value
\bar{k}	forward rate constant (mol m ⁻³ s ⁻¹)	1.81
logK _g	apparent equilibrium constant for glass	N/A ¹
η	pH power law coefficient	0.35
E _a	activation energy of glass dissolution reaction	68
r _x	Na ion-exchange rate (mol m ⁻² s ⁻¹)	3x10 ⁻⁹

¹Dissolution rate not limited by equilibrium with any aqueous species

Table IV. Aqueous species identified by EQ3/6 simulations of K-26 waste glass dissolution in groundwater

AlO ₂ ⁻	CO ₂ (aq)	KSO ₄ ⁻	NaHCO ₃ (aq)
B(OH) ₃ (aq)	CO ₃ ²⁻	Mg ²⁺	NaHPO ₄ ⁻
BO ₂ ⁻	Cs ⁺	MgB(OH)/	NaHSiO ₃ (aq)
Ca ²⁺	H ⁺	MgCl ⁺	NaOH(aq)
CaB(OH) ₄ ⁺	H ₂ PO ₄ ⁻	MgCO ₃ (aq)	NaSO ₄ ⁻
CaCl ⁺	H ₂ SiO ₄ ²⁻	MgHCO ₃ ⁺	O ₂ (aq)
CaCO ₃ (aq)	HAIO ₂ (aq)	MgHPO ₄ (aq)	OH ⁻
CaHCO ₃ ⁺	HPO ₄ ²⁻	MgPO ₄ ⁻	Pb ²⁺
CaHPO ₄ (aq)	HSKV	MgSO ₄ (aq)	PO ₄ ³⁻
CaOH ⁺	K ⁺	MoO ₄ ⁻	SiO ₂ (aq)
CaPO ₄ ⁻	KCl(aq)	NaB(OH) ₄ (aq)	Sn(OH) ₄ (aq)
CaSO ₄ (aq)	KHPO ₄ ⁻	NaCl(aq)	SO ₄ ²⁻
Cl	KOH(aq)	NaCO ₃ ⁻	

Eq. (1) is an approximation for glass because glass is metastable and the reaction proceeds one way (i.e., glass dissolves). Two of the unknown parameters in Eq. (1) (E_a , and η) have been determined for LAWABP1 [4] glass. In addition, test results with LAWABP1 glass (and most other ILAW glasses) show that it is susceptible to a secondary reaction mechanism, alkali ion exchange. This reaction results in the selective extraction of sodium via a reaction:



where LAWABP1-Na represents the unreacted glass containing sodium and LAWABP1-H represents a hydrated glass where the sodium has been replaced with an equimolar amount of hydrogen. STORM keeps track of the amount of hydrated glass formed via Eq. (2) and then allows it to dissolve according to the same kinetic rate law as the parent glass.

RESULTS

A STORM simulation of the 14-year field experiment is currently under development. Although there is a large list of aqueous and mineral species to consider, placing all of these species in a STORM input file would almost certainly result in a simulation that would not converge due to the complexity of the reaction network. Preliminary results have been obtained by assuming K-26 glass is dissolving at the forward rate of reaction. This means that the rate of glass dissolution depends only on the pH, and is unaffected by $\text{SiO}_2(\text{aq})$ concentrations. A secondary mineral observed during vapor hydration tests, Na_2SiO_3 , does not precipitate at the average field temperature of 11°C. A comparison of the steady-state model effluent concentrations with average sample concentrations from a control borehole and the K-26 field experiment facility are shown in Fig. 8.

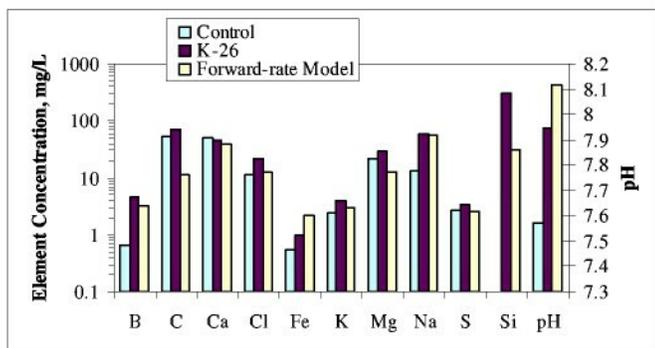


Fig. 8. Comparison of Model Effluent Concentrations with Sample Values from a Control Borehole and the K-26 Waste Glass Field Experiment

The forward rate constant for K-26 (Table VI) was estimated by fitting modeled to measured values of boron, the species most likely to act as a tracer. Concentrations of $\text{B}(\text{OH})_3(\text{aq})$ throughout the model domain are shown for reference. Although $\text{B}(\text{OH})_3(\text{aq})$ concentrations are high inside the small cracks of the glass, dilution by water flowing around the block results in lower concentrations at the outflow drain (Fig. 9). Observed concentrations of aqueous Si are much greater than those of model predictions; no control values are available for comparison. In the current simulation, Si concentrations are being buffered by the precipitation of silicate minerals originally present in the sand filler, such as Illite and Smectite. It may be necessary to suppress some of these minerals to match measured values of $\text{SiO}_2(\text{aq})$. Total C concentrations are lower than those observed; because biological sources of subsurface carbon have not been included in this model.

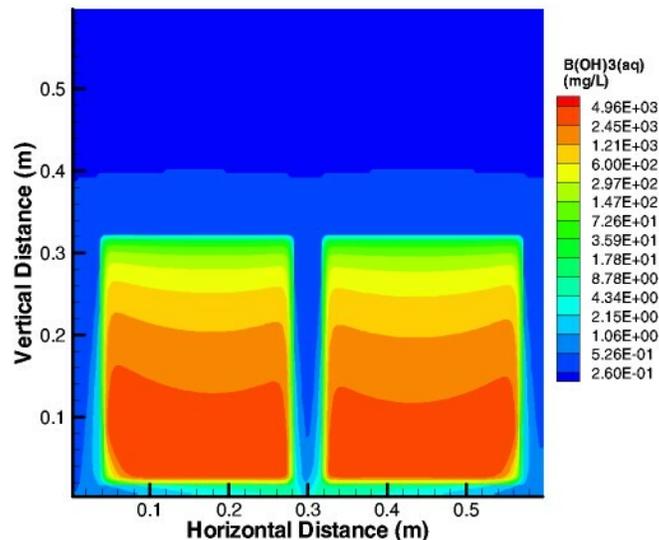


Fig. 9. Steady-state $\text{B}(\text{OH})_3(\text{aq})$ Concentrations Predicted by STORM Simulation of K-26 Glass Dissolving at the Forward-Rate of Reaction

The ion exchange rate (Table VI) was determined by fitting modeled Na^+ concentrations to observed values (Fig. 8). Of the total amount of aqueous Na produced by the glass, 40% comes from glass dissolution and 60% from sodium ion exchange. Normalizing the total glass dissolution rate by the total amount of glass initially present in the model yields a glass mass loss rate of 0.006% per year. When glass kinetic parameters are available from single-pass flow-through laboratory experiments, currently underway, they will be compared to these predictions from field experiments.

ACKNOWLEDGMENTS

Financial support provided by CH2M Hill Hanford Group, Inc. under contract DE-AC06-76RLO 1830. The simulations were performed using the MSCF in the William R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the DOE's Office of Biological and Environmental Research and located at PNNL.

REFERENCES

- [1] Sobolev, I.A., A.S.Barinov, M.I.Ojovan, N.V.Ojovan, I.V.Startceva, G.N.Tchuikova, Z.I.Golubeva, and A.V.Timopheeva, *Long-Term Tests Of Low And Intermediate Level Waste Packages Under Field And Experimental Repository Conditions*. 2001, Scientific and Industrial Association <Radon>: Moscow, Russia.
- [2] Ojovan, M.I., I.V. N.V. Ojovan, G.N. Startceva, Z.I. Tchuikova, Golubeva, and A.S. Barinov, *Waste glass Behavior in Loamy Soil of a Wet Repository Site*. J. Nucl. Mat., 2001. 298: p. 174-179.
- [3] Mann, P.M., RJ. Puigh, II, C.R. Eiholzer, Y. Chen, N.W. Kline, A.H. Lu, B.P. McGrail, P.O. Rittmann, G.F. Williamson, N.R. Brown, and P.E. LaMont, *Hanford Immobilized Low Activity Tank Waste Performance Assessment*. 1998, Project Hanford Management Contractor: Richland, Washington. p. 682.
- [4] McGrail, B.P., D.H. Bacon, J.P. Icenhower, W.L. Ebert, P.P. Martin, H.T. Schaef, and E.A. Rodriguez, *Waste Form Release Data Package for the 2001 Immobilized Low-Activity Waste Performance Assessment*. 2001, Pacific Northwest National Laboratory: Richland, Washington, p. 80
- [5] McGrail, B.P. and D.H. Bacon, *Selection of a Computer Code for Hanford Low-Level Waste Engineered-System Performance Assessment*. 1998, Pacific Northwest National Laboratory: Richland, Washington.
- [6] Bacon, D.H., M.D. White, and B.P. McGrail, *Subsurface Transport Over Reactive Multiphases (STORM): A General, Coupled, Nonisothermal Multiphase Flow, Reactive Transport, and Porous Medium Alteration Simulator, Version 2, User's Guide*. 2000, Pacific Northwest National Laboratory: Richland, Washington, p. 201.
- [7] Arya, L.M. and J.F. Paris, *A physicoempirical model to predict the soil moisture characteristic from panicle-size distribution and bulk density data*. Soil Sci. Soc. Am. J., 1981.45: p. 1023-1030.
- [8] Campbell, G.S., *Soil Physics with BASIC: Transport Models for Soil-Plant Systems*. 1985, New York: Elsevier.
- [9] van Genuchten, M.T., *RET.C.F77: Program to Analyze Observed Soil Water Retention and Hydraulic Conductivity Data*. 1985, U.S. Salinity Laboratory Special Report: Riverside, California.
- [10] White, M.D. and M. Oostrom, *STOMP: Subsurface Transport Over Multiple Phases, Theory Guide*. 1996, Pacific Northwest National Laboratory: Richland, Washington.