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Experimental Study and Reactive Transport Modeling of Boric Acid Leaching of Concrete

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Abstract. Borated water leakage through spent fuel pools (SFPs) at pressurized water reactors is a concern because it could cause corrosion of reinforcement steel in the concrete structure, compromise the integrity of the structure, or cause unmonitored releases of contaminated water to the environment. Experimental data indicate that pH is a critical parameter that determines the corrosion susceptibility of rebar in borated water and the degree of concrete degradation by boric acid leaching. In this study, reactive transport modeling of concrete leaching by borated water was performed to provide information on the solution pH in the concrete crack or matrix and the degree of concrete degradation at different locations of an SFP concrete structure exposed to borated water. Simulations up to 100 years were performed using different boric acid concentrations, crack apertures, and solution flow rates. Concrete cylinders were immersed in boric acid solutions for several months and the mineralogical changes and boric acid penetration in the concrete cylinder were evaluated as a function of time. The depths of concrete leaching by boric acid solution derived from the reactive transport simulations were compared with the measured boric acid penetration depth.

1 Introduction

Spent fuel pools (SFPs) at pressurized water reactors are seismically qualified concrete structures that have stainless steel liners and contain borated water, maintain spent fuel temperatures, and provide radiation shielding. Long-term borated water leakage through the SFP liners is a concern because it could degrade the concrete and corrode the reinforcement steel [1]. The corrosion products could cause cracks in the concrete to form or propagate, which could compromise the integrity of the structure or cause unmonitored releases of contaminated water to the environment.

Solution pH is a critical parameter that determines the corrosion susceptibility of rebar in borated water and the degree of concrete degradation by boric acid [$B(OH)_3$] leaching. Measured rebar corrosion rate is low (~1 μm/yr or less) when the solution pH is ~7.1 or higher but increases with decreasing pH and can reach ~100 μm/yr in solutions with pH less than ~6.7 [2]. Borated water that leaks through the SFP liner initially will be acidic, but as it diffuses into the concrete pores or flows through the concrete joints or cracks, it will react chemically with the cement matrix and the solution pH will increase. Higher pH will decrease the susceptibility of rebar to corrosion and of concrete to leaching. If borated water pH was known at different points along a flow path, an assessment could be performed on the susceptibility to degradation of rebar and concrete at different locations of an SFP concrete structure. However, it is impracticable to measure the pH of borated water in the pore spaces, joints, or cracks of SFP concrete structures.

To provide information on the pH of borated waters and the degree of concrete degradation that could occur at different locations of an SFP concrete structure, reactive transport modeling of concrete leaching by borated water was performed in this study. Reactive transport models combine chemical reactions, such as dissolution and precipitation, with hydrodynamic processes, such as water flow, diffusion, and dispersion, and can account for changes in porosity, permeability, and flow properties of the porous medium due to dissolution and precipitation reactions. Leaching experiments also were conducted in which concrete cylinders were immersed in boric acid solutions and the mineralogical changes and boric acid penetration were evaluated as a function of time. The measured penetration depths were compared with the results of the reactive transport calculations.

2 Boric Acid Leaching Experiment

Concrete cylinders (10.2-cm diameter × 20.3-cm length) were prepared and cured for at least 28 days in capped plastic cylinders. The concrete mix design is shown in Table 1. Six cylinders were immersed at room temperature in boric acid solutions—three in 1,200 ppm B solution and three in 2,400 ppm B solution. All the solutions were refreshed continuously using peristaltic pumps.

At 180, 240, and 300 days, one cylinder was removed from each solution for petrographic analysis. Sections were sawcut perpendicular to the long axis of the cylinder and were lapped on a steel wheel with progressively finer silicon carbide grit. The lapped sections were then examined under a stereomicroscope at 7× to 100× magnification. The depth of the affected cement paste was measured in each specimen at a 10× magnification using a micrometer in the microscope eyepiece. The depth of the affected cement paste also was determined by spraying phenolphthalein—a pH-indicating solution—on the lapped surfaces of the specimens. When phenolphthalein is applied to concrete, the cement paste will turn pink at a pH above 9, but will remain colorless at lower pHs. Therefore, the depth of the uncolored cement paste will indicate the depth to which the acid has affected the cement paste.

3 Reactive Transport Modeling

Reactive transport modeling of boric acid leaching of concrete under saturated flow conditions was conducted using the reactive transport codes X1t and X2t, which are part of the Geochemist's Workbench (GWB) suite of software for simulating groundwater transport and chemical reactions in geochemical systems [3]. The 1-dimensional (1-D) X1t simulations are relevant to situations in which diffusion is the mechanism whereby boric acid solution penetrates a reinforced concrete structure, whereas the 2-dimensional (2-D) X2t simulations are relevant to situations in which boric acid solution leaks from a spent fuel pool, flows in a crack, and diffuses into the concrete matrix.

Table 1. Concrete mix design (batch weights per cubic meter)

Material	Weight (kg)
CEMEX Type I/II Cement	332
5/8" River Rock	1,305
Silica Sand	573
Water	153 (117 L)
Air Content	1.5±1.5%
Concrete Properties: Compressive strength at 28 days = 27.6 MPa; Water/Cement Ratio = 0.46; and Slump = 7.6±2.5 cm	

Table 2. Solid phases in concrete [Ref. 4]

Solids	Volume %	Solids	Volume %
Aggregate†	72	Hydrogarnet	1.67
Calcium-silicate-hydrate ($CSH_{1.8}$)	8.3	Hydrotalcite	0.46
Portlandite	4.7	Hematite	0.33
Ettringite	3.2		
†Wang's (2009) [4] concrete model used calcite aggregate. In this study, aggregate was represented by rutile.			

The mineral phases and their relative amounts assumed to be present in the concrete are based on the study by Wang (2009) [4] and are listed in Table 2. Calcium-silicate-hydrate (CSH) is the most dominant cement mineral, followed by portlandite, ettringite, hydrogarnet, and hydrotalcite. Iron oxide was represented by the mineral hematite.

Granite initially was assumed to comprise the concrete aggregate. However, granite rock is much less reactive to borated water compared to the minerals present in hydrated cement. To simplify the model, boric acid interaction with the aggregate was assumed to be negligible and the aggregate in the model was represented by the relatively insoluble mineral rutile (TiO_2). Kosakowski, et al. (2009) [5] employed a similar approach and used SnO_2 to represent inert components in their cement model. Values of concrete porosity and pore diffusion coefficient were set equal to 0.07 and 1×10^{-6} cm^2/s, respectively [4].

The X1t and X2t simulations used the thermodynamic database *thermo.com.v8.r6+.dat*, which was developed at the Lawrence Livermore National Laboratory [3]. Thermodynamic data on cement minerals were added and data on a few other minerals were revised. The added and revised data are listed in Ref. [2]. The CSH phase dissolves incongruently and its dissolution could be modeled most accurately using a solid solution model. However, it is more common to model CSH dissolution as a process involving a series of CSH phases with different Ca/Si mole ratios, each phase with its own characteristic thermodynamic properties. The latter approach was used in this study because X1t and X2t have no option for using solid solution models. Three CSH phases, with Ca/Si mole ratios of 1.8, 1.1, and 0.8, were added to the database. The CSH phase initially present in the concrete was represented by $CSH_{1.8}$. CSH dissolution results in decalcification (i.e., the formation of CSH phases with lower Ca/Si ratio such as $CSH_{1.1}$ and $CSH_{0.8}$).

Because diffusion is a slow process, it was sufficient for the 1-D simulations to use a 1-cm long model domain, which was divided into 50 equal length grids. The 2-D simulations, which included both advective and diffusive processes, required a larger model domain. The cracked concrete was represented by two blocks, 130-cm long and 7-cm wide, separated by a crack of uniform aperture. Because of symmetry, only one of the blocks and half of the crack aperture were included in the model domain (Figure 1). In the x-direction, the block length was divided into 20 nonuniform grids, with a denser grid near the inlet (left) side where more chemical alteration is expected, and a coarser grid farther along the flow path (toward the right). In the y-direction, the 7-cm block width was divided into seven nonuniform grids, with a denser grid near the crack and a coarser grid farther away from the crack. One row of 20 cells along the bottom of the concrete block represented the

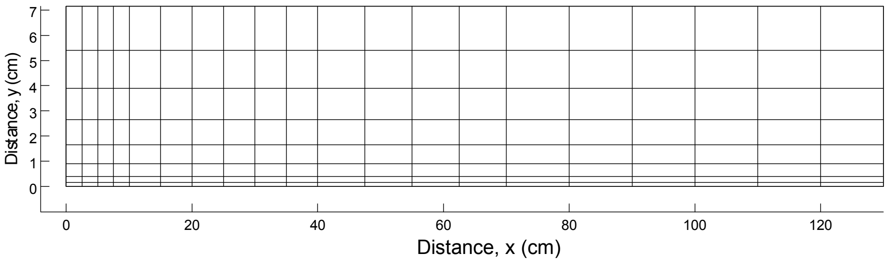


Fig. 1. Grid spacing used in the 2-D reactive transport model

crack. A total of 160 cells were used in the 2-D model, including the 20 cells representing the concrete crack.

The 1-D simulations assumed initial boron concentrations of 1,200 and 2,400 ppm to determine the effect of boric acid concentration on concrete leaching and to enable a comparison of model results with the leaching data. The 2-D simulations assumed an initial boron concentration of 2,400 ppm. To determine the effect of crack aperture, concrete crack half-apertures of 0.15, 0.25, and 0.5 cm were specified. The solution flow rate also was varied by specifying two values of flow rate (termed “specific discharge”—the volume of solution flowing per unit time through a unit cross-sectional area of the porous medium) on the inlet side equal to 0.2 and 1.0 $cm^3/cm^2 \cdot day$. The volume of solution exiting the crack per unit time can be calculated from the values of specific discharge derived from the model, the input crack half-aperture, and an assumed crack length.

In the absence of information on crack lengths in an actual SFP concrete structure, a 1-m crack length was assumed in the 2-D simulations in order to calculate the solution volume exiting the crack at various half-apertures and inlet flow rate. The calculated values are tabulated in Table 3. To put these calculated values into perspective, the leakage that is occurring through the east wall of the Fuel Handling Building of the Salem Nuclear Generating Station (New Jersey, U.S.A.) has been estimated to be 473 cm^3/day [6]. The calculated flow rate of boric acid solution exiting the crack in Simulations 4, 5, and 6 is more than three times that estimated to be leaking from the Salem Fuel Handling Building. Thus, the X2t simulations reasonably approximate the borated water flow rate that has been observed in an SFP concrete structure. To determine the effect of a much higher flow rate, an additional simulation (Simulation 7) was performed with a solution volume exiting the crack that is 12 times higher than what has been observed at the Salem Fuel Handling Building.

The 1-D and 2-D simulations assumed local equilibrium and a temperature of 25 °C, and were conducted for time periods up to 100 years. The 1-D model results include solution pH in the concrete matrix, concrete mineralogy, and matrix porosity. Additional model results for the 2-D simulations include solution pH in the concrete crack and specific discharge at the crack outlet (volume of solution flowing per unit time through a unit cross-sectional area of the crack).

4 Results

4.1 Petrographic analyses and boric acid leaching depth

Petrographic examination of the concrete specimens indicated that the cement paste affected by boric acid leaching is very soft, highly porous, and retains very little inherent strength [2]. The affected paste exhibits a color change from grey to white in some specimens or to yellowish in others. There is a distinct transition from the weak, porous, affected cement paste to the dense, unaffected cement paste. In some specimens, the severely affected cement paste is underlain by a dark colored, competent cement paste layer, below which is a thin white layer of weak cement paste.

Phenolphthalein solution testing showed that the acid attack has affected the cement paste to the depth of the thin, white layer of weakened cement paste. The depth affected by boric acid leaching

Table 3. Matrix of 2-D simulations and calculated volumetric flow rate exiting the concrete crack

Simulation Number	Inlet Specific Discharge ($cm^3/cm^2 \cdot day$)	Crack Half-Aperture (cm)	Calculated Specific Discharge at Crack Outlet ($cm^3/cm^2 \cdot day$)	Volumetric Flow Rate for 1-m-Long Crack (cm^3/day)
1	0.2	0.15	9.54	286
2	0.2	0.25	5.80	290
3	0.2	0.5	3.00	300
4	1.0	0.15	47.7	1,431
5	1.0	0.25	29.0	1,450
6	1.0	0.5	15.0	1,500
7	4.0	0.15	190.7	5,721

Table 4. Measured boric acid leaching depth compared with X1t-calculated values

Reaction Time (days)	Leaching Depth in 1,200 ppm B Solution		Leaching Depth in 2,400 ppm B Solution	
	Measured*	**Calculated†**	**Measured**	**Calculated**
180	0.5 to 1.1 mm (Ave. = 0.75 mm)	0.78 mm	0.6 to 1.2 mm (Ave. = 0.85 mm)	1.24 mm
240	1.0 to 1.5 mm (Ave. = 1.31 mm)	0.86 mm	1.2 to 1.7 mm (Ave. = 1.42 mm)	1.32 mm
300	1.4 to 1.8 (Ave. = 1.61 mm)	0.95 mm	1.4 to 1.8 (Ave. = 1.60 mm)	1.49 mm

*Data on specimens immersed in boric acid solutions at room temperature. Average of 20 measurements
†Derived from X1t reactive transport simulations using pH 8.5 as the criterion for leaching depth

is tabulated in Table 4. The affected depths increased with time and solution concentration. The rate of boric acid leaching, as with other concrete degradation mechanisms, depends in part on the rate of diffusive transport.

4.2 X1t simulation results

Figure 2 illustrates the X1t-calculated concrete mineralogy as a function of distance into the concrete matrix after 44 and 300 days of reaction with 2,400 ppm B solution. With increasing time, the dissolution front moves deeper into the concrete, resulting in portlandite dissolution, CSH decalcification (indicated by a transition from $CSH_{1.8}$ to $CSH_{1.1}$), and formation of a leached layer, which is dominated by quartz, hematite, and hydrotalcite and is likely to have very little inherent strength. Quartz was used to represent the residual silica remaining after cement minerals have been dissolved. Although CSH decalcification is more likely to produce amorphous silica instead of quartz, convergence problems were encountered in some GWB simulations when amorphous silica was used.

Figure 3 shows the X1t-calculated concrete pore solution pH and porosity as function of depth from the concrete surface and time of reaction with the 2,400 ppm B solution. The pH of the solution, initially 4.95, increases quickly to alkaline values as the solution diffuses into and reacts with the cement matrix. Boric acid penetration into the concrete matrix is faster at 2,400 ppm B compared to 1,200 ppm B (data not shown) due to the higher concentration gradient. In Figure 3(b), the porosity is high close to the concrete surface due to almost complete dissolution of the cement minerals. For example, the 44-day porosity profile shown in Figure 3(b) indicates that a 0.03-cm-thick leached layer has formed with a porosity greater than 0.23. Porosity decreases with increasing

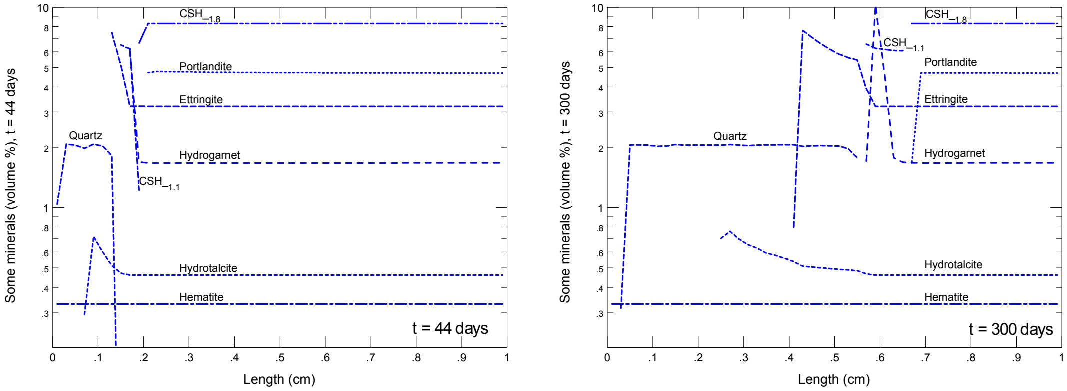
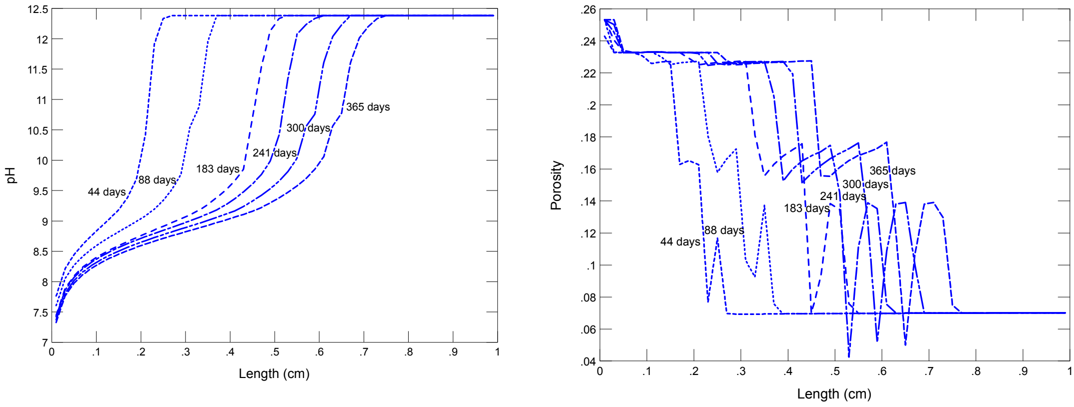


Fig. 2. X1t-calculated mineralogy (vol %) as a function of distance into the concrete matrix after 44 and 300 days of reaction with 2,400 ppm B solution. Aggregate remained constant at 72 vol % and is not shown.



(a) **(b)**

Fig. 3. X1t-calculated (a) pore solution pH and (b) concrete porosity versus depth after various time periods of reaction with 2,400 ppm B solution. The initial pH and porosity were 4.95 and 0.07, respectively.

depth due to lesser dissolution of cement minerals, eventually attaining the initial porosity of 0.07, but localized increases in porosity occur due to reprecipitation of ettringite and hydrogarnet.

As described in a preceding section, the depth of concrete leaching was determined by petrographic examination or with the aid of a phenolphthalein test method. When phenolphthalein is applied to concrete, the cement paste will turn pink at a pH above ~9 and will remain uncolored at pH values below ~8. To compare the X1t results with the measured leaching depths, the concrete depths at which the pore solution pHs are equal to 8.5 were derived from the X1t results and listed in Table 4. The X1t model underpredicts the leaching depth in 1,200 ppm B solution at 240 and 300 days and slightly overpredicts the leaching depth in 2,400 ppm B solution at 180 days. However, considering the general uncertainties in the model parameters and in the limited experimental data, the agreement between calculated and measured leaching depths is relatively good.

4.3 X2t simulation results

An example of X2t-calculated pH of concrete pore solutions is illustrated in Figure 4. The pore solution pH, initially 13.5, decreases as the boric acid solution flows in the crack and diffuses into the matrix. With increasing time, the decreased pH propagates deeper into the concrete matrix. Other data (not shown) indicate that the pH decrease is accelerated by an increase in inlet flow rate.

An example of X2t-calculated pH evolution with time and distance from the crack inlet of a boric acid solution flowing in a concrete crack is shown in Figure 5. The solution pH, initially 4.95, rises to neutral values within a few centimeters of the inlet, at least during the first 30 years. At later times, it takes longer flow distances in the crack before the boric acid solution is neutralized. At distances from the inlet of 20 cm or more, the solution pH in the crack remains higher than the threshold pH (~7.1) for rebar corrosion at time periods up to 100 years.

Figure 6 shows X2t-calculated solution pH in the concrete matrix as functions of time and distance from the concrete crack. Close to the crack inlet [x = 3.75 cm], the pH in the concrete

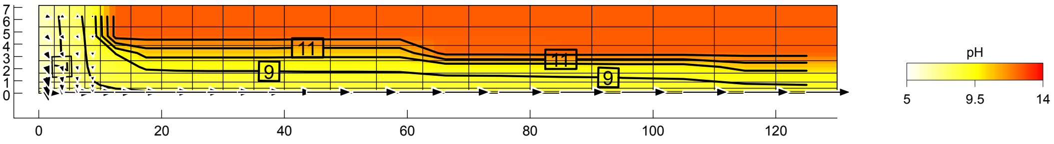


Fig. 4. X2t-calculated concrete pore solution pH at 40 years. Boron solution (2,400 ppm, initial pH = 4.95) enters the left side of the model domain, flows in the crack (0.15-cm half-aperture) at the bottom, diffuses into the concrete matrix, and exits the right side of the domain. Inlet specific discharge = 0.2 $cm^3/cm^2 \cdot day$.

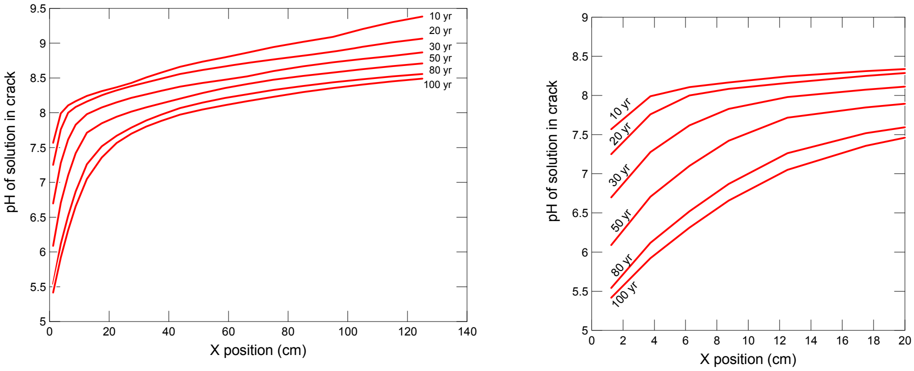


Fig. 5. X2t-calculated pH of solution flowing in the concrete crack as a function of time and distance (x) from the inlet. The figure on the right shows solution pHs within 20 cm of the inlet. Crack half-aperture = 0.25 cm. Inlet specific discharge = 0.2 $cm^3/cm^2 \cdot day$.

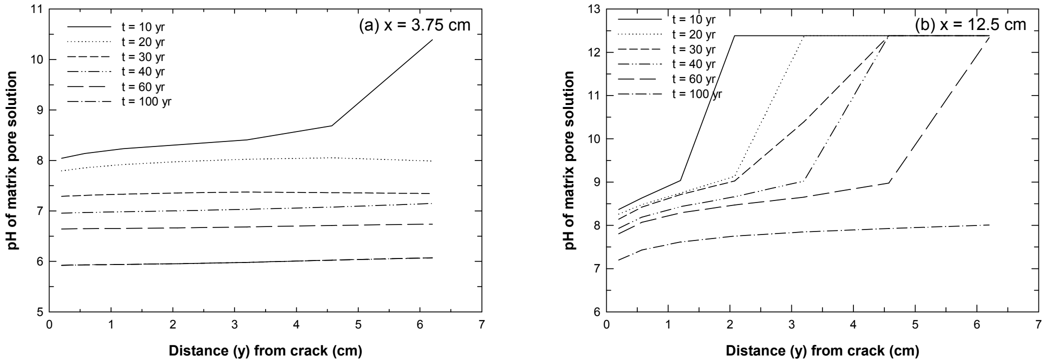


Fig. 6. X2t-calculated solution pH in concrete matrix as a function of time, distance (y) from the crack, and distance (x) from the inlet. A typical thickness of rebar concrete cover is 5.1 cm. Crack half-aperture = 0.25 cm. Inlet specific discharge = 0.2 $cm^3/cm^2 \cdot day$.

matrix is maintained above the threshold pH for rebar corrosion up to 30 years. At later times, further diffusion of the boric acid solution reduces the concrete matrix pH to less than the threshold value. Farther away from the crack inlet, boric acid diffusive transport into the concrete matrix is delayed such that at 12.5 cm from the crack inlet the matrix pH is maintained above the threshold pH for rebar corrosion even after 100 years.

Figure 7 plots X2t-calculated concrete porosity as functions of time, distance (y) from the crack, and distance (x) from the inlet. The figure shows that the concrete porosity is high close to the concrete crack due to almost complete dissolution of the cement minerals and formation of a leached layer. The porosity decreases with increasing distance from the crack due to lesser dissolution of cement minerals, eventually attaining the initial porosity of 0.07. At 100 years of simulation time, a leached layer thicker than the typical concrete cover of 5.1 cm has formed near the crack inlet [x = 12.5 cm].

5 Implications to Boric Acid Corrosion of Rebar in Concrete

Rebar corrosion data indicate that the threshold pH for carbon steel corrosion in borated solution is between 6.8 and 7.3 [2]. The corrosion rate is low [~1 μm/yr or less] when the solution pH is ~7.1 or higher. Below pH ~7.1, the corrosion rate increases with decreasing pH and can reach ~100 μm/yr in solutions with pH less than ~6.7. The potential for reinforcement steel corrosion can be evaluated

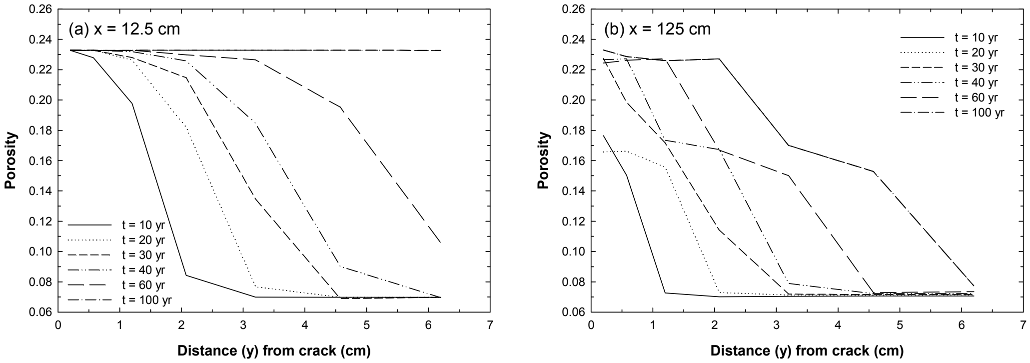


Fig. 7. X2t-calculated concrete porosity as a function of time, distance (y) from the crack, and distance (x) from the inlet. Initial concrete porosity = 0.07. Crack half-aperture = 0.15 cm. Inlet specific discharge = 0.2 $cm^3/cm^2 \cdot day$.

by comparing the concrete pore solution pH calculated using X1t and X2t with the threshold pH for corrosion. Figure 8 shows the calculated pore solution pH in concrete that was reacted with 2,400 ppm B solution. The values were calculated using the X1t code and are relevant to an intact concrete whereby diffusion is the mechanism for boric acid penetration. As shown in Figure 8, in such a system the pore solution pHs are above the threshold pH (~7.1) for rebar corrosion even after 70 years of reaction. Thus, the results indicate that reinforcement steel with a 5.1-cm concrete cover is unlikely to undergo corrosion to time periods of at least 77 years, if diffusion is the mechanism by which borated water penetrates the concrete.

In systems where borated water penetrates the concrete structure through cracks, the 2-D reactive transport simulations indicate that rebar close to the crack inlet, whether exposed in the crack or covered by concrete, can become susceptible to corrosion. Simulation results presented in this paper and additional ones described in Ref. [2] indicate that this susceptibility will depend on the concrete aperture and solution flow rate, in addition to solution concentration. At the lowest flow rate used in the simulations, the boric acid solution is quickly neutralized, exceeding the threshold pH (~7.1) for rebar corrosion within ~4 cm of the inlet even after 30 years of flow. At a higher flow rate approximately similar to that of borated water leakage at the Salem Fuel Handling Building, it takes a longer flow distance [~12 cm] to increase the solution pH in the crack above the rebar corrosion threshold pH at 30 years. At a flow rate 12 times higher than that observed at the Salem Fuel Handling Building, it takes approximately 30 cm before the threshold pH is exceeded at 30 years. Thus, rebar exposed in the crack close to the borated water inlet could be susceptible to corrosion.

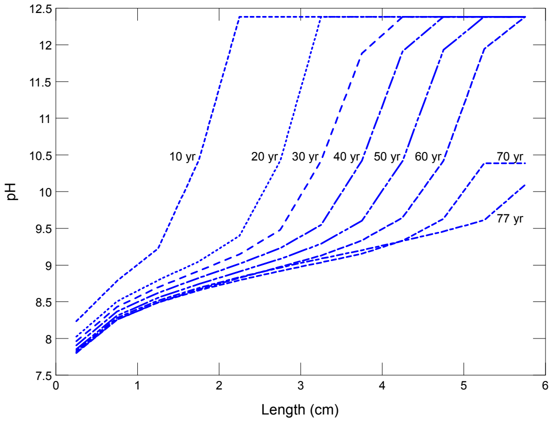


Fig. 8. X1t-calculated concrete pore solution pH versus concrete depth after various reaction times with 2,400 ppm B solution

Rebar exposed in the crack farther from the inlet would be less susceptible to corrosion, but would become more susceptible to corrosion with increasing flow duration. Similarly, rebar embedded in the concrete but close to the flow inlet would be the most susceptible to corrosion. At the lowest flow rate used in the simulation, rebar close to the inlet [x = 3.75 cm] would be protected from corrosion for 30 years, but could be subject to corrosion afterwards. Rebar embedded in concrete and located farther away from the inlet would be less subject to corrosion. However, increases in flow rate and flow period would result in increased dissolution, increased porosity, and decreased solution pH in the concrete. Thus, the concrete cover may provide little protection to rebar embedded in concrete but located near the inlet if the boric acid flow rate is high enough and/or the flow duration is long enough.

6 Conclusions

1-D and 2-D reactive transport simulations were conducted to determine the degree of concrete dissolution and pH change that may occur as boric acid solution diffuses into the matrix or flows in the crack of a reinforced concrete structure. The depth of concrete leaching by boric acid solution derived from the 1-D model agree relatively well with the measured leaching depths in concrete specimens that were immersed in boric acid solutions for up to 300 days. The 1-D simulation results indicate that leaching by boric acid solution diffusing into concrete is mitigated by the acid-neutralizing capacity of the cement minerals such that reinforcement steel with a 5.1-cm [2-in] concrete cover is unlikely to undergo corrosion for at least 77 years. The 2-D simulation results indicate that concrete provides significant chemical reactivity to neutralize the acidic pH of borated water that may leak from an SFP, flow into a crack in the SFP concrete structure, and diffuse into the concrete matrix. However, reinforcement steel close to the crack inlet, whether exposed in the crack or covered by concrete, can become susceptible to corrosion depending on the crack aperture, solution flow rate and duration, and boric acid concentration.

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