

DEVELOPING A KINETIC LEACHING MODEL FOR SOLIDIFIED/STABILIZED HAZARDOUS WASTES

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Summary

Leaching mechanisms in the pozzolanic-based solid matrix are controlled by the free hydrogen ions available in the leachant. Alkalinity leached is the consequence of the penetration of hydrogen ions. Hydrogen ions diffuse into the solid matrix and neutralize the alkalinity provided by the binder in the leach front. pH decreases after the acid neutralization (buffer) capacity is consumed. The metals precipitated previously in high-pH environment are dissolved again and diffuse outward into the leachant. A friable, silica-rich leached layer has been formed and moves deeper into the solid matrix with time. At early stages of leaching, an "unsteady diffusion with fast chemical reaction" model can be used to predict the acid penetration in the pozzolanic-based paste.

Introduction

Chemical stabilization/solidification is common practice in the disposal of radioactive waste. In recent years this method has been applied to treatment of hazardous materials.

Several generic treatment systems have been used. The pozzolanic- or portland cement-based treatment systems show potentially useful application for wastes containing heavy metals. The mixing of pozzolanic-based binders with wastes converts heavy metals in the waste to insoluble hydroxides and silicates which are entrapped within the solid paste. It also is believed that some metals may be physically bound to the paste lattice. Permeability coefficients of the solidified waste matrices were comparable to those of clay, ranging from 10^{-6} to 10^{-7} cm/s [1].

The potential impact on the environment of solid wastes disposed on land is most frequently assessed and predicted from bench-scale laboratory leaching tests. In order to do this effectively, predictive mathematical models must be used.

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Short term leachability studies of solidified low-level radioactive wastes [2] and solidified hazardous wastes [3] show diffusion to be the dominant factor governing leaching rate. A semi-infinite medium diffusion model with uniform initial concentration and zero surface concentration can be used to interpret the kinetic data generated from serial batch leaching tests [2]. The equation takes the form:

$$\frac{\sum a_n}{A_0} \frac{V}{S} = 2 \frac{D_e^{0.5}}{\pi} t_n^{0.5} \quad (1)$$

where a_n is contaminant loss during leaching period n (mg), A_0 initial amount of contaminant present in the specimen (mg), V volume of specimen (cm^3), S surface area of specimen (cm^2), t_n time to end of leaching period n (s), and D_e effective diffusion coefficient (cm^2/s).

Leachate generation is an extremely complex process. The free alkalinity present in the pozzolanic-based paste maintains a high-pH environment and limits the metal leachability of fixed wastes [4]. Calcium hydroxide, which is produced by the hydration reactions of binder, provides most of the buffering capacity. The leaching model shown above, however, does not include the factor of acid strength of the leachant and cannot describe the penetration depth of leaching front into the waste solids.

This paper shows the relationship of the hydrogen ion in the leachant, the penetration depth of leaching front, and the alkalinity leached from the solid matrix. Using these results, kinetic leaching models are developed.

Method and material

Six binder combinations were prepared by mixing three different, pozzolanic-based binders at two different water/binder ratios according to ANSI/ASTM standards. Samples were cast as 23.5 mm diameter by 25.6 mm height cylinders. Sample types are summarized in Table 1. In the rest of this discussion, samples will be referred to by their sample numbers shown in the table.

Dynamic leaching test procedures were followed. A 20-to-1 leachant/solid ratio was used. Five specimens of each binder combination were leached at each of two different strengths of acetic acid solution, 5 and 15 milliequivalents per gram of dry sample. The leachants were renewed at 25, 45, 70, 91, and 117 h for the cement kiln dust and lime-fly-ash samples; 26, 104, 340, 531, and 681 h for the portland cement samples. Calcium hardness titration and pH measurement were determined for each contacted solution. Physical measurements included the dimensions and the wet and dry weights of each sample before as well as after leaching. One sample was removed for physical measurement at each renew schedule. During each contact, an outer layer of friable leached product with distinct texture/color difference was observed on each specimen. The kernel, which is the unfriable part of the specimen, was ob-

TABLE 1

Binder type	Water/binder ratio	Leachant strength (meq/g)	Sample no.
Cement kiln dust	0.50	15	KD50-15
		5	KD50-5
	0.65	15	KD65-15
		5	KD65-5
50% Lime, type N ^a 50% Fly-ash, type F	0.35	15	LF35-15
		5	LF35-5
	0.50	15	LF50-15
		5	LF50-5
Type I portland cement	0.33	15	PC33-15
		5	PC33-5
	0.45	15	PC45-15
		5	PC45-5

^aDolomitic hydrated lime.

tained by physically scrubbing off the friable outer layer. Physical measurements included weighing before and after drying and measuring the dimensions of the oven-dried kernel with a micrometer gauge.

Results and discussion

Acid attacks pozzolanic-based paste through permeation of pore structure and dissolution of ions that must diffuse back through a chemically altered layer to enter solution. Acid consumes most of the calcium hydroxide in the leached layer and leaves a highly porous structure. Diffusion across this layer can be considered as a steady-state process. At the leaching front, diffusion of hydrogen ions proceeds as if the medium is infinite and dissolution reactions occur simultaneously in the pores. Proton transfer reactions are usually very fast with half-lives less than milli-seconds [5]. Hence, the dissolution reactions can be treated as diffusion-controlled fast reactions. The whole process then can be described as steady-state diffusion across the leached layer and unsteady-state diffusion-controlled fast reactions in the porous leaching front.

Figures 1 through 3 show the cumulative amount of calcium hardness leached from solidified/stabilized samples plotted versus the square root of time for cement kiln dust, lime-fly-ash, and portland cement binder systems, respectively. Figures 4 through 6 show the penetration distance of the leaching front versus the square root of time for the same samples.

Two acetic acid strengths were used as the leachants — 5 and 15 meq or mmol acetic acid per gram of solids leached. Figures 1 through 3 show that the 15 meq/g leachant leached considerably more hardness than the 5 meq/g leachant. The figures also show that the lower water/binder ratio samples leached

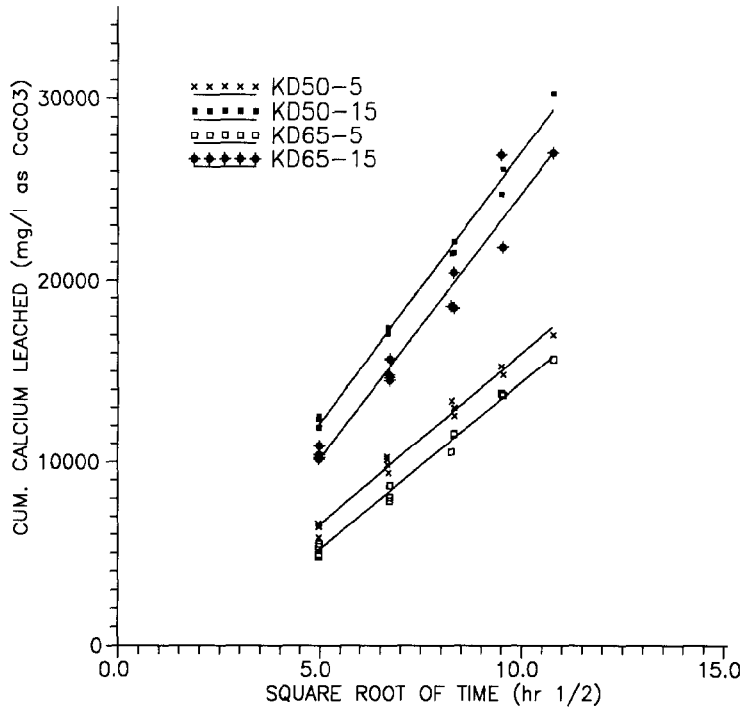


Fig. 1.

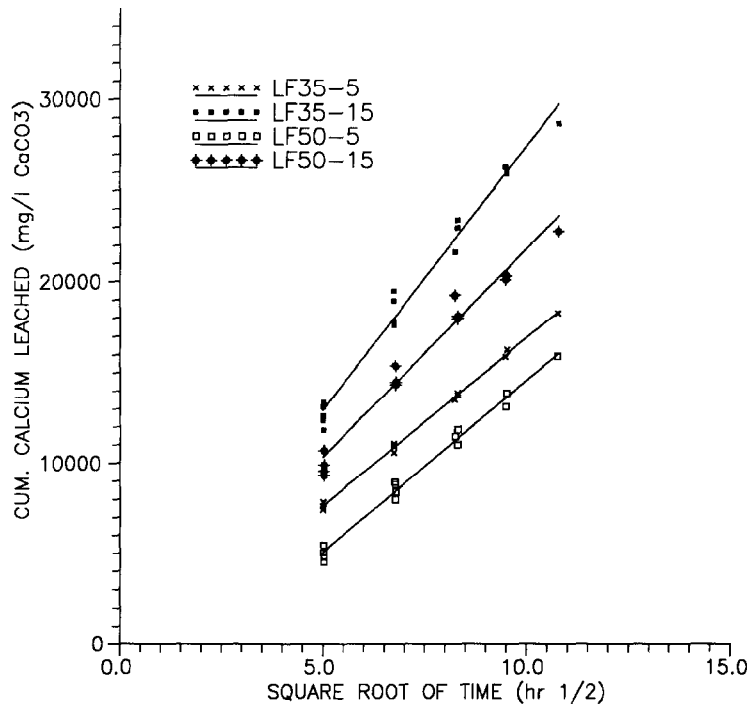


Fig. 2.

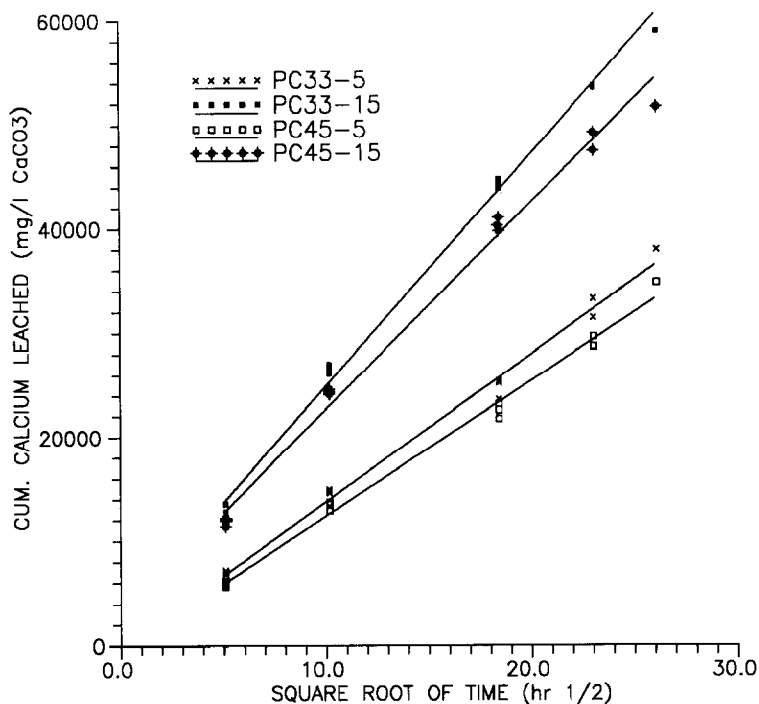


Fig. 3.

more in a given acid strength leachant than ones with a higher water/binder ratio. These results are as expected. Figures 4 through 6 show that the distance of penetration of the leaching front is highly dependent on the leachant acid strength. The leachant with 15 meq acidity/g solids advanced into the solids much more rapidly than did the weaker leachant. Water/binder ratio had little or no effect on penetration distance or rate of penetration. This indicates that acid penetrating into the solids and metal leaching from the solids are controlled by different mechanisms.

Figure 7 shows predicted ratios based on least squares regression of calcium hardness leached at 5 meq/g and 15 meq/g based, and Fig. 8 shows ratios of penetration distance at the two acid strengths for each time interval. Figure 7 shows that the 15 meq/g leachant consistently leaches approximately 1.65 times as much hardness as the 5 meq/g leachant, for all binders and at all water/binder ratios. Figure 8 indicates that the penetration distance for the 15 meq/g leachant is approximately 2.0 times that for the weaker leachant.

At this moment a numerical solution to the problem of combined acid penetration and resultant metal leaching seems premature. Appropriate assumptions need be made to approach the answer. For gas-solid systems, a steady-state diffusion across the product layer with chemical reactions at the bound-

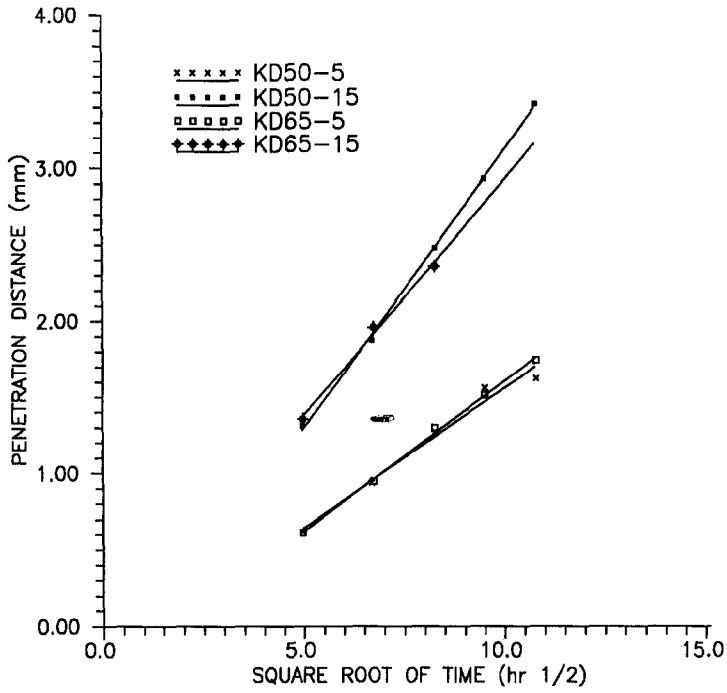


Fig. 4.

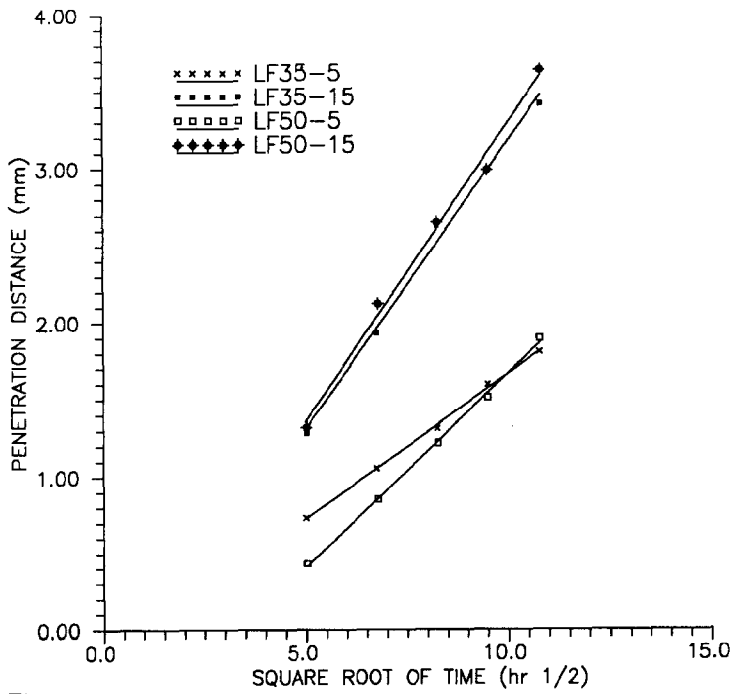


Fig. 5.

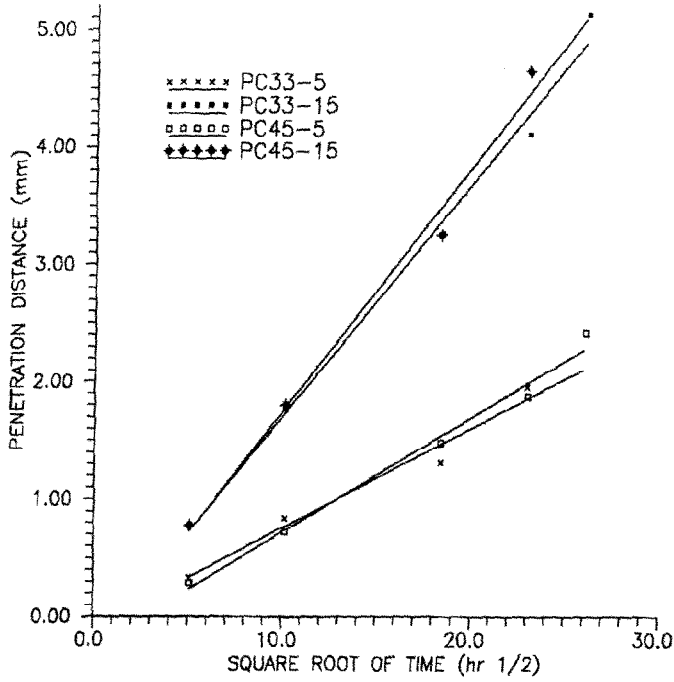


Fig. 6.

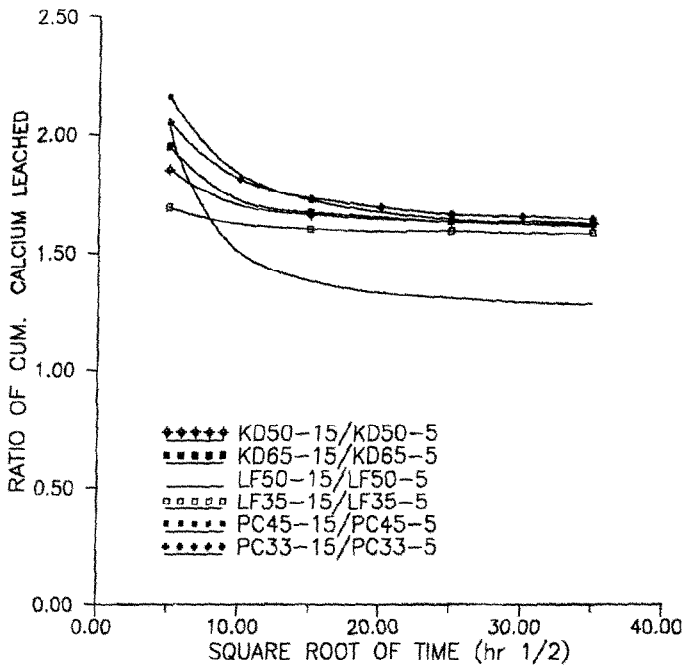


Fig. 7.

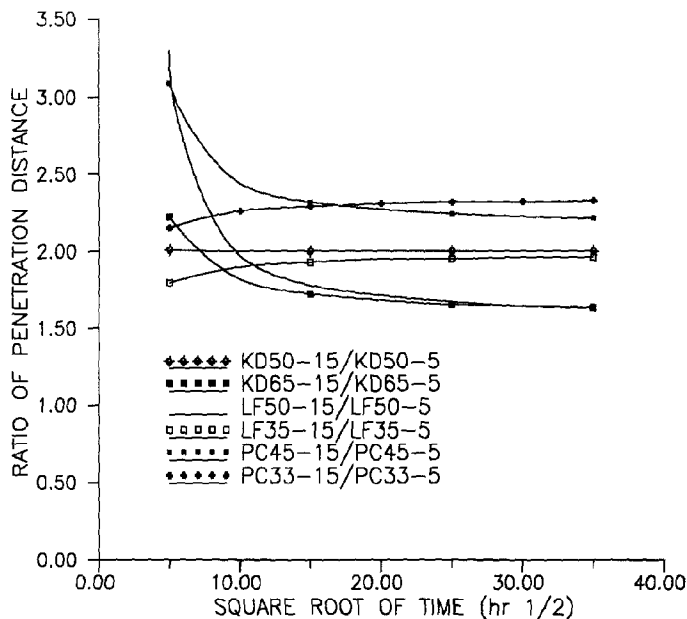


Fig. 8.

ary is often assumed. The pseudo-steady-state assumption, however, is only valid in gas-solid systems if the gas density is about a thousandth of the solid density. For liquid-solid systems this assumption may be in error [6].

When non-porous solid dissolves in acid, the dissolution can be idealized as three sequential steps. In the first step, acid and other reagents diffuse to the surface; in the second, they react with the surface; in the third, the dissolved solid diffuses away from the surface. The overall dissolution rate depends on the sum of the resistances of diffusion and of reaction. However, the pozzolanic-based paste is a porous material and the dissolution is more complicated than that of non-porous solids because diffusion and reactions occur simultaneously within the whole leaching zone [7].

It is the authors' opinion that the phenomenon can be simplified as "unsteady diffusion with fast chemical reactions" at the early stage of leaching when the friable layer is fairly thin. Further work should be done to find the limitations. In the following the model is discussed.

Unsteady-state diffusion

The solution of the problem of diffusion from a solid, the surface concentration of which is maintained constant, into a semi-infinite medium, having zero initial concentration, involves only the single dimensionless parameter $z/\sqrt{4D_e t}$, where z is the penetration distance. It follows from this that:

- (1) The depth of penetration of any given concentration is proportional to the square root of time.
- (2) The amount of diffusing substance entering the medium through unit area of its surface (flux) varies as the square root of time [8].

The concentration of diffusing substance $C(z,t)$ and the flux of diffusion $J(z,t)$ are given by:

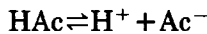
$$C(z,t) = C_0 [1 - \operatorname{erf}(z/\sqrt{4D_e t})] \quad (2)$$

$$J(z,t) = C_0 (\sqrt{D_e/\pi t}) \exp(-z^2/4D_e t) \quad (3)$$

where erf is the error function and C_0 the initial bulk concentration of the diffusing substance.

Ionization of weak acid

The free hydrogen ions available in the leachant may be the most important factor governing leaching rate because H^+ has a diffusion coefficient which is approximately one order of magnitude higher than the other species. Acetic acid is considered a weak acid and is not completely ionized in dilute solutions. The ionization reaction of acetic acid can be illustrated as:



$$[\text{H}^+][\text{Ac}^-]/[\text{HAc}] = K_a = 1.75 \times 10^{-5} \quad \text{at } 25^\circ\text{C, 1 bar}$$

where Ac^- is used to designate the acetate ion and HAc the acetic acid and K_a is the ionization constant. If C_0 is the initial molar concentration of acetic acid in the solution and x is the molar concentration of the acetic acid ionized to form H^+ and Ac^- ions, then:

$$[\text{HAc}] = (C_0 - x) \text{ mol/l}$$

$$[\text{H}^+] = [\text{Ac}^-] = x \text{ mol/l}$$

$$K_a = [\text{H}^+][\text{Ac}^-]/[\text{HAc}] = x^2/(C_0 - x)$$

At room temperature, the value of x is very small compared to the value of C and the ionization constant K_a can be approximated to yield the well known result:

$$\begin{aligned} K_a &\approx x^2/C_0 \\ x &\approx \sqrt{K_a C_0} \end{aligned} \quad (4)$$

Equation 4 shows that the hydrogen ion concentration is proportional to the square root of initial acetic acid concentration. For the two acetic acid strengths used in this research, 15 meq/g and 5 meq/g, the ratio of hydrogen ion concentration becomes $\sqrt{(15/5)}$, which is approximately 1.73. This suggests that the concentration of free hydrogen ions in the aqueous solution controls the pen-

etration of the reaction front and can be considered an independent variable for the leaching mechanism [9]. Figure 7 shows that the amount of calcium leached in the 15 meq/g leachant was 1.7 times greater than in the 5 meq/g leachant. This is in complete agreement with the above discussion.

Based on the experimental results presented earlier, the penetration depth and the accumulative hardness leached follow linear relationships versus square root of time. Penetration distance is obtained from averaging original dimension and height minus kernel dimension and height. The penetration distance versus square root of time can be interpreted as representing the free hydrogen ions diffusing into the solid matrix, and the accumulative hardness versus square root of time as the dissolved metal ions diffusing out of the solid matrix.

Acid neutralization capacity

Acid neutralization capacity (ANC) is determined by conducting separate extractions of several predried, crushed, waste samples with leaching solutions of varying levels of acidity [10]. It can be defined as the amount of acidity neutralized by a given quantity of sample to a certain pH range with the unit mole/mass and can be obtained by running the ANC test [11]. It has been used to determine the buffering capacity of the stabilized/solidified waste form. For cement-based wastes, ANC is generally about 15 meq/g to bring the pH down from 12.5 to 9 [12].

Simplified mathematical model

A mathematical equation can be derived to describe the penetration distance r by combining eqn. (3) and the concept of acid neutralization capacity. To do this, we first write a mass balance on a thin layer Δz , located at some arbitrary position z within the semi-infinite medium with constant cross sectional area A . The mass balance of hydrogen ions in this layer is:

$$(A\Delta zC_H)/t = A(J|_z - J|_{z+\Delta z}) + r_H A \Delta z$$

$$\left(\begin{array}{c} \text{Hydrogen ion} \\ \text{accumulation} \end{array} \right) = \left(\begin{array}{c} \text{H}^+ \text{ diffusion in} \\ \text{minus that out} \end{array} \right) + \left(\begin{array}{c} \text{amount H}^+ \text{ produced} \\ \text{by chemical reactions} \end{array} \right) \quad (5)$$

where C_H denotes the concentration of hydrogen ions, $J|_z$ and $J|_{z+\Delta z}$ the flux of hydrogen ions at z and $z + \Delta z$, respectively. The net rate of hydrogen ions produced per volume, r_H , can be explained as the hydrogen ions produced by ionization of weak acid minus the hydrogen ions consumed by neutralization of alkalinity per unit volume. If the ANC of a given sample can be expressed as a function of hydrogen ion concentration, $ANC = f(C_H)$, then by definition, r_H can be expressed as the negative rate of acid neutralization capacity changed, $-\partial \Theta f(C_H) / \partial t$, where Θ is the density of the sample with a unit mass/volume. Equation (5) now becomes:

$$\partial(A\Delta z C_H)/\partial t = A(J|_z - J|_{z+\Delta z}) - A\Delta z[\partial\Theta f(C_H)/\partial t] \quad (6)$$

By dividing both sides by $A\Delta z$, this becomes:

$$\frac{\partial C_H}{\partial t} = \frac{\partial}{\partial z} \left(D_e \frac{\partial C_H}{\partial z} \right) - \frac{\partial \Theta f(C_H)}{\partial t} \quad (7)$$

The diffusion coefficient D_e used here is not the true diffusion coefficient, but is referred to as the effective diffusion coefficient because diffusion takes place in the liquid filling interstices of the porous matrix. The liquid path length (tortuosity) can be much longer than that assumed in the formulation of Fick's law. Type of binder and water/binder ratio play the most important roles in determination of the porosity of the solidified mixture.

If the effective diffusion coefficient D_e and the density Θ can be assumed constants, the above equation becomes:

$$\frac{\partial C_H}{\partial t} = \frac{D_e}{[1 + \Theta f'(C_H)]} \frac{\partial^2 C_H}{\partial z^2} \quad (8)$$

where $f' = \partial f / \partial C_H$.

One more restriction must be placed on the system before a simple analytical solution can be obtained: $f(C_H)$ is assumed to be first order, that is, $f(C_H) = KC_H$. With the following boundary conditions:

$$t=0, \quad \text{all } z, \quad C_H \approx 0$$

$$t>0, \quad z=0, \quad C_H = C_0$$

$$z=\infty, \quad C_H \approx 0$$

the solution is:

$$C_H(z,t) = C_0 [1 - \text{erf}(z\sqrt{(1+\Theta K)/4D_e t})] \quad (9)$$

$$J(z,t) = C_0 [\sqrt{D_e(1+\Theta K)/\pi t}] \exp[-z^2(1+\Theta K)/4D_e t] \quad (10)$$

The concentration of hydrogen ions at any given distance and given time can be obtained by solving eqn. (9). The pH profile along the penetration distance can then be established.

Conclusions

Leaching mechanisms in the pozzolanic-based solid matrix are controlled by the free hydrogen ions available in the leachant. Alkalinity leached is the consequence of the penetration of hydrogen ions. Hydrogen ions diffuse into the solid matrix and neutralize the alkalinity provided by the binder in the leach front. pH decreases after the acid neutralization capacity is consumed. The metals precipitated previously in high-pH environment are dissolved again

and diffuse outward into the leachant. A friable, silica-rich leached layer has been formed and moves deeper into the solid matrix with time. At early stages of leaching, an "unsteady diffusion with fast chemical reaction" model can be used to predict the acid penetration in the pozzolanic-based paste.

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