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Cement and Concrete Research 33 (2003) 1917–1924

CEMENT AND CONCRETE RESEARCH

Modeling the transport of multiple corrosive chemicals in concrete structures: Synergetic effect study

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Received 23 May 2001; accepted 26 February 2003

Abstract

The synergetic effect of multiple corrosive chemicals in concrete structures has been investigated using a mathematical model with a set of one-dimensional linear diffusion equation that belongs to the equation of continuity. Combining the method of Laplace transform with the substitution method, and using the convolution theorem, the analytical solution of the one-dimensional linear diffusion equation can be solved. Based on the equation of continuity and the reduction of corrosive chemical concentration through the mechanical driving force with second-order kinetics, a system of transport equations may be employed to elucidate the synergetic effect of two contaminants such as Cl^- and CO_2, Cl^-, and SO_4^{2-}, and CO_2 and SO_4^{2-}. The computer package "Mathematica" was used to show the synergetic effect of multiple corrosive chemicals in concrete structures. The numerical results of concrete structure subjected to multiple corrosive chemicals shed some light on the synergistic behavior of Cl^- and CO_2, Cl^-, and SO_4^{2-}, and CO_2 and SO_4^{2-} versus their individual behavior. These results prove that the proposed model may really describe the synergetic effect of multiple corrosive chemicals in concrete structures. However, it is still recommended that experiments should be performed to choose suitable parameters for numerical simulations.

Keywords: Carbon dioxide; Chloride ion; Corrosion; Sulfate ion; Synergetic effect

1. Introduction

Haken [1] pointed out that synergetics deals with systems composed of many subsystems, which may be of quite different natures, such as electrons, atoms, molecules, cells, neurons, mechanical elements, photons, organs, animals, or even humans. Many concrete structures have recently been constructed all over the world. The environmental attack of the usually high-deterioration rate in these structures, due to the corrosion of the concrete members, has attracted considerable attention.

Reinforcing bars (rebars) in concrete are protected from corrosion by a thin oxide layer that forms on the surface of the rebar in the high-pH ($pH > 12.5$), aqueous pore solution in concrete. Corrosion may start when this protective layer is destroyed in the presence of corrosive chemicals such as chloride, CO_2, and sulfate ions. These corrosive chemicals reduced the pH value of concrete to values below 9. These corrosive chemicals have been identified as constituents of concrete mixes used in this part of the world.

There are much more interesting studies regarding the chloride attached to concrete [2–11], as well as the effect of physical–chemical attacks on the evolution of stress–strain states into RC (reinforced concrete) structures [12]. Prezzi et al. [13] pointed out that corrosion of steel in concrete is usually associated with one or more of the following: penetration of chloride ions, carbonation, penetration of acids, such as sulfur dioxide gas (SO_2), and bacterial action. Loo et al. [14] described that SO_2 may reduce the pH of cement paste. SO_2 concentration in the atmosphere is many thousands of times lower than that of CO_2, and its effect is significant only in a heavily polluted environment. Therefore, the main corrosive chemical process responsible for the neutralization of cement paste is carbonation. Somuah et al. [15] obtained the experimental results to shed some light on the synergistic behavior of sulfate and carbonate ions versus their individual behavior by using AC impedance spectroscopy. Papadakis et al. [16] made a description of the synergetic effect between chloride and carbon dioxide

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doi:10.1016/S0008-8846(03)00081-4

penetration in concrete structures, i.e., chloride action is accelerated by carbonation. Saetta et al. [17] indicated that a complete service-life model might incorporate the synergetic effect of multiple corrosive chemicals (e.g., chloride attack and carbonation). Feldman et al. [18] stated that the concurrent presence of sulfate and chloride ions in solution decreased the chloride ion ingress rate into ordinary Portland cement concrete and concrete incorporating the partial replacement of the cement with slag and silica fume. Tumidajski and Chan [19] denoted that the synergistic effect of sulfate ion on chloride ingress is different in Portland cement concrete and concrete incorporating partial replacement of Portland cement by slag. It was found that sulfate and CO_2 decrease the chloride penetration and diffusivity in the ordinary Portland cement concrete, whereas the opposite behavior is observed for the slag concrete. To date, however, no studies have attempted to model the synergetic effect of multiple corrosive chemicals in concrete structures using a mathematical model. This is a notable shortcoming, because the use of Fick's second law in previous studies may have resulted in underestimation of service-life prediction due to corrosion damage.

This article evaluates the synergetic effect of chloride, CO_2, and sulfate ions in concrete using a mathematical model with a system of one-dimensional linear diffusion equations. The results shed some light on the synergetic effect of chloride, CO_2, and sulfate ions versus their individual behavior. This research may provide a useful reference for researchers attempting to consider accelerated corrosion concept through synergetic effect of multiple corrosive chemicals.

2. Mathematical modeling of synergetic effect

Assume that retardation factor, $R=1$ (both the deterioration ingredient and pore water in concrete have the same transport velocity), and the first-order mechanical driving force, $K_T C$, is firstly considered. The governing equation describing the one-dimensional transport phenomena of concrete corrosion is

$$\frac{\partial C}{\partial t} = D_\mathrm{s}\frac{\partial^2 C}{\partial x^2} - \nu\frac{\partial C}{\partial x} - K_T C \tag{1a}$$

with initial and boundary conditions

$$C(x,0) = C_\mathrm{i} \tag{1b}$$

$$C(0,t) = C_\mathrm{s} \tag{1c}$$

$$C(L,t) = C_\mathrm{f} \tag{1d}$$

where C is the concentration of corrosive chemicals, C_i, C_s, and C_f are the initial concentration of contaminants in concrete, on the surface of the concrete structures, and at the interface between the concrete and rebar, respectively, D_s is the diffusion coefficient, ν is the average velocity in pore water in concrete, K_T is the rate of constant for first-order decay at a given temperature T, L is the concrete cover thickness of the rebar, x is space, and t is time.

The first, second, and third terms of the right-hand side of Eq. (1a) represent the diffusion, pore, and chemical reaction effects, respectively. Adopting the method of Laplace transform associated with the substitution method and the convolution theorem to obtain the analytical solution of Eqs. (1a)–(1d), the analytical solution of Eqs. (1a)–(1d) can be expressed in terms of

$$\begin{aligned} C(x,t) = {} & \mathrm{e}^{\frac{\nu}{2D_\mathrm{s}}x - \frac{\nu^2+4K_T D_\mathrm{s}}{4D_\mathrm{s}}t} \int_0^t \frac{x}{2\sqrt{\pi D_\mathrm{s}\tau^3}}\mathrm{e}^{-\frac{x^2}{4D_\mathrm{s}\tau}} \\ & \times \left(C_\mathrm{s}\mathrm{e}^{\frac{\nu^2+4K_T D_\mathrm{s}}{4D_\mathrm{s}}(t-\tau)} - C_\mathrm{i}\mathrm{e}^{\frac{\nu^2}{4D_\mathrm{s}}(t-\tau)} \right)\mathrm{d}\tau + C_\mathrm{i}\mathrm{e}^{-K_T t} \end{aligned} \tag{2}$$

If we consider the retardation factor, R (both the deterioration ingredient and pore water in concrete do not have the same transport velocity), for the corrosive chemicals, then Eq. (1a) should be rewritten as follows:

$$\frac{\partial C}{\partial t} = \frac{D_\mathrm{s}}{R}\frac{\partial^2 C}{\partial x^2} - \frac{\nu}{R}\frac{\partial C}{\partial x} - \frac{K_T}{R}C \tag{3}$$

with initial and boundary conditions the same as Eqs. (1b)–(1d).

The analytical solution of Eq. (3) is

$$\begin{aligned} C(x,t) = {} & \mathrm{e}^{\frac{\nu}{2D_\mathrm{s}}x - \frac{\nu^2+4K_T D_\mathrm{s}}{4D_\mathrm{s}R}t} \int_0^t \frac{x}{2\sqrt{\pi D_\mathrm{s}\tau^3/R}}\mathrm{e}^{-\frac{x^2 R}{4D_\mathrm{s}\tau}} \\ & \times \left(C_\mathrm{s}\mathrm{e}^{\frac{\nu^2+4K_T D_\mathrm{s}}{4D_\mathrm{s}R}(t-\tau)} - C_\mathrm{i}\mathrm{e}^{\frac{\nu^2}{4D_\mathrm{s}R}(t-\tau)} \right)\mathrm{d}\tau + C_\mathrm{i}\mathrm{e}^{-K_T t/R} \end{aligned} \tag{4}$$

To set up the mathematical model for describing the synergetic effect of concrete structures subjected to multiple

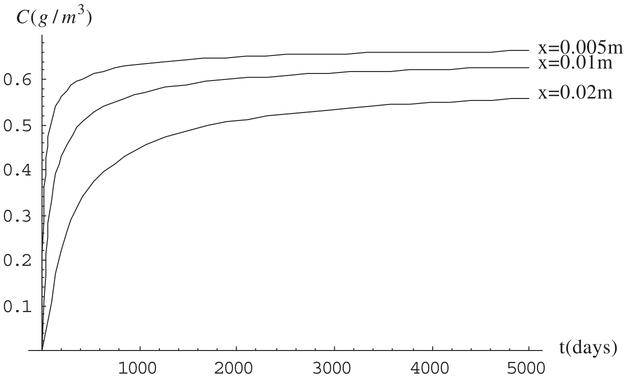

Fig. 1. Concentration–time relationships of CO_2.

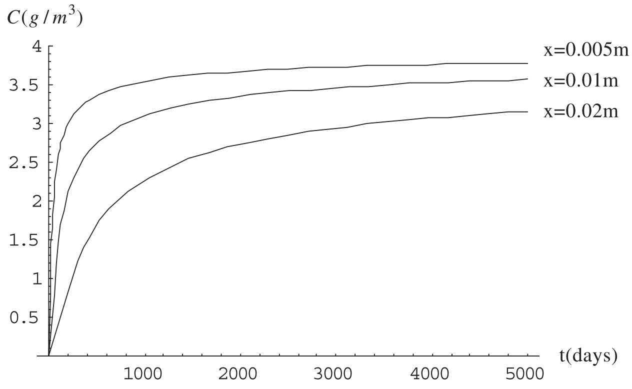

Fig. 2. Concentration–time relationships of Cl^- under $R_{Cl^-} = 0.8$.

corrosive media attack, we first consider the completely equivalent binary diffusion equations [20]

$$\frac{\partial \rho_A}{\partial_t} + (\nabla \cdot \rho_A \nu) = (\nabla \cdot \rho D_{AB} \nabla w_A) + r_A \tag{5}$$

$$\frac{\partial C_A}{\partial_t} + (\nabla \cdot C_A \nu^*) = (\nabla \cdot M_t D_{AB} \nabla x_A) + R_A \tag{6}$$

where ρ_A is the mass concentration of species A, ρ is the total mass density, ν is the mass average velocity in pore water in concrete, w_A is the mass fraction of species A, r_A is the mass rate of production of species A, $D_{AB} = D_{BA}$ is the binary diffusivity for system A–B based on free energy driving force, C_A is the molar concentration of species A, M_t is the total molar concentration, ν^* is the molar average velocity in pore water in concrete, x_A is the mole fraction of species A, R_A is the molar rate of production of species A, and ∇ is the "del" or "nabla" operator. Both Eqs. (5) and (6) are the equations of continuity. The physical meaning is the law of conservation of mass.

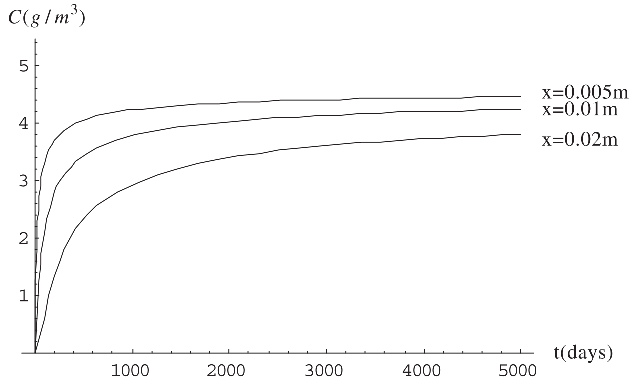

Fig. 3. Concentration–time relationships of synergetic effect for $Cl^- + CO_2$ under $R_{Cl^-} = R_{CO_2} = 0.8$.

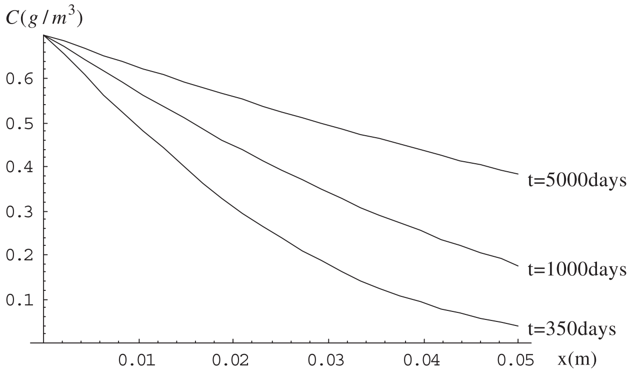

Fig. 4. Concentration–carbonation depth relationships.

Either one of Eq. (5) or (6) describes the concentration profiles in a binary diffusing system. The only restriction is the absence of thermal pressure and forced diffusion. Eqs. (5) and (6) are valid for systems with variable ρ and variable D_{AB}. Because Eqs. (5) and (6) are fairly general, they are also fairly unwieldy. In the analysis of diffusing systems, we can often legitimately assume either constant ρ or constant molar density, and thereby effect some simplification. Assume that both ρ and D_{AB} in Eq. (5) are constant. For this assumption, Eq. (5) becomes

$$\frac{\partial \rho_A}{\partial t} + \rho_A(\nabla \cdot \nu) + (\nu \cdot \nabla \rho_A) = D_{AB} \nabla^2 \rho_A + r_A \tag{7}$$

For a fluid of constant ρ, we have

$$\nabla \cdot \nu = 0 \tag{8}$$

When Eq. (7) is divided by M_A, we get

$$\frac{\partial C_A}{\partial t} + (\nu \cdot \nabla C_A) = D_{AB} \nabla^2 C_A + R_A \tag{9}$$

The reduction of corrosive chemicals concentration (i.e., the concentration gradient), which is a kind of physical

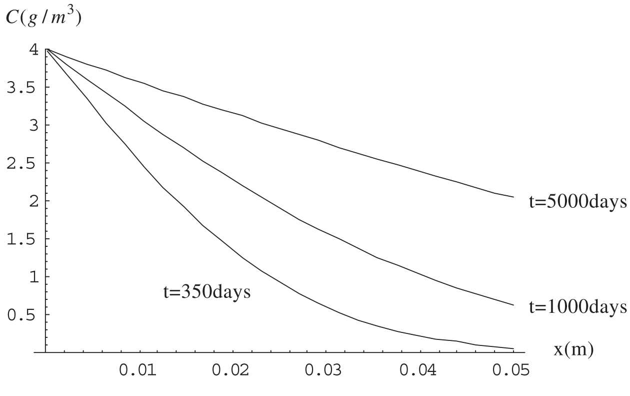

Fig. 5. Concentration–chlorination depth relationships under $R_{Cl^-} = 0.8$.

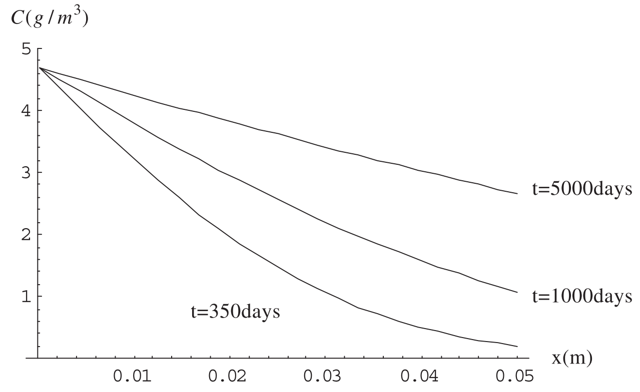

Fig. 6. Concentration–penetration depth of synergetic effect for $Cl^- + CO_2$ under $R_{Cl^-} = R_{CO_2} = 0.8$.

phenomenon with mechanical driving force [21], can be expressed as

$$\frac{\Delta C}{\Delta t} = \begin{cases} K_T & \text{(zero order)} \\ K_T C & \text{(first order)} \\ K_T C^2 & \text{(second order)} \\ M_t \mu_{\max}\left(\frac{C}{K_C + C}\right) & \text{(mixed order)} \end{cases} \tag{10}$$

where C is the corrosive chemical concentration, M_t is the total molar concentration, $\mu_{\max}$ is the maximum corrosive chemical utilization rate per unit mass concrete structure, K_C is the corrosive chemical half-saturation constant, and Δt is the time interval being considered.

The zero, first, and second order of the right-hand side of Eq. (10) denote that the nth power of C (i.e., C^n) have $n = 0$, $n = 1$, and $n = 2$, respectively. As for the mixed order, this means that the power of C is a kind of mixed type. Eq. (10) displays the relationship between C and t. The zero, first, and second order represented in Eq. (10) have the constant, linear, and parabolic value in the C–t curve, respectively. As to the mixed order, first, C has an initial value at $t = 0$, and then approximately reaches a constant value as t increases. Based on this mathematical point of view, the application on each mechanism for Eq. (10) is independent on the C–t curve, which is an experimental result obtained from concrete structure subjected to deterioration ingress. It is worthy to point out that the first, second, and mixed order represented in Eq. (10) are usually used in the case of single, synergetic, and ground water contamination effects, respectively.

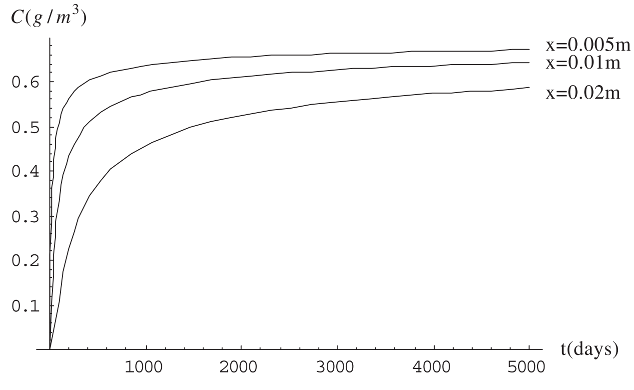

Fig. 7. Concentration–time relationships of CO_2.

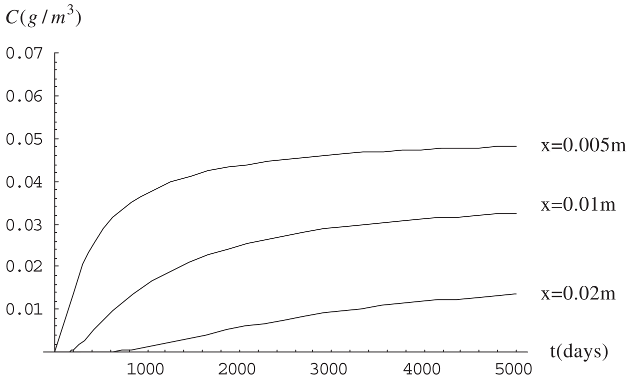

Fig. 8. Concentration–time relationships of SO_4^{2-} under $R_{SO_4^{2-}} = 0.8$.

Based on Eqs. (1a)–(1d) and (3) and Eqs. (6), (9), and (10), we obtain a system of partial differential equations with initial and boundary conditions due to both Cl^- and CO_2 penetrating into the concrete structure [21]:

$$\frac{\partial C_{Cl^-}}{\partial t} = \frac{D_s}{R_{Cl^-}} \frac{\partial^2 C_{Cl^-}}{\partial x^2} - \frac{\nu}{R_{Cl^-}} \frac{\partial C_{Cl^-}}{\partial x} - \frac{1}{R_{Cl^-}} K C_{Cl^-} C_{CO_2} \tag{11}$$

$$\frac{\partial C_{CO_2}}{\partial t} = D_s \frac{\partial^2 C_{CO_2}}{\partial x^2} - \nu \frac{\partial C_{CO_2}}{\partial x} - K C_{Cl^-} C_{CO_2} \tag{12}$$

$$\frac{\partial M_s}{\partial t} = \frac{D_s}{R_C} \frac{\partial^2 M_s}{\partial x^2} - \frac{\nu}{R_C} \frac{\partial M_s}{\partial x} + M_s K' C_{Cl^-} C_{CO_2} \tag{13}$$

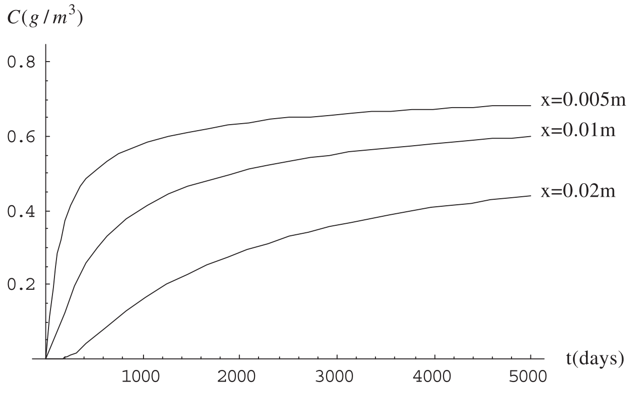

Fig. 9. Concentration–time relationships of synergetic effect for $SO_4^{2-} + CO_2$ under $R_{SO_4^{2-}} = R_{CO_2} = 0.8$.

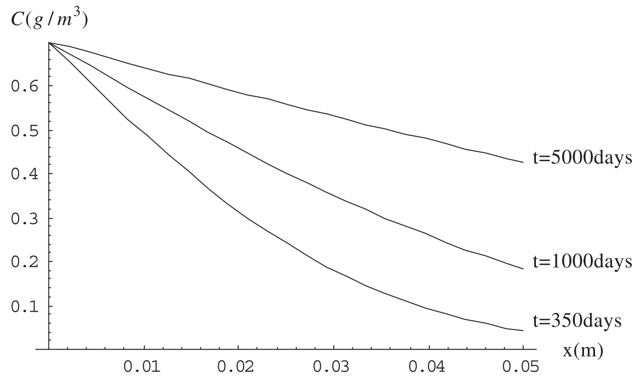

Fig. 10. Concentration–carbonation depth relationships.

$$C(x,0) = C_{\mathrm{i,Cl^-}} \quad C(x,0) = C_{\mathrm{i,CO_2}}$$

$$M_{\mathrm{s}}(x,0) = M_{\mathrm{i,ms}} \quad x > 0 \tag{14}$$

$$C(0,t) = C_{\mathrm{s,Cl^-}} \quad C(0,t) = C_{\mathrm{s,CO_2}}$$

$$M_{\mathrm{s}}(0,t) = M_{\mathrm{s,ms}} \quad t > 0 \tag{15}$$

$$C(L,t) = C_{\mathrm{f,Cl^-}} \quad C(L,t) = C_{\mathrm{f,CO_2}}$$

$$M_{\mathrm{s}}(L,t) = M_{\mathrm{f,ms}} \quad t > 0 \tag{16}$$

where $R_{\mathrm{Cl^-}}$ is the retardation factor for chlorination, R_{C} is the corrosive chemical retardation factor, K and K' are the corrosive chemical half saturation constant, $C_{\mathrm{i,Cl^-}}$ and $C_{\mathrm{i,CO_2}}$ are the initial concentrations of $\mathrm{Cl^-}$ and $\mathrm{CO_2}$ in concrete, respectively, $C_{\mathrm{s,Cl^-}}$ and $C_{\mathrm{s,CO_2}}$ are the $\mathrm{Cl^-}$ and $\mathrm{CO_2}$ concentration on the surface of the concrete structures, respectively, $C_{\mathrm{f,Cl^-}}$ and $C_{\mathrm{f,CO_2}}$ are the $\mathrm{Cl^-}$ and $\mathrm{CO_2}$ concentration at the interface between the concrete and rebar, respectively, $C_{\mathrm{Cl^-}}$ and $C_{\mathrm{CO_2}}$ are the $\mathrm{Cl^-}$ and $\mathrm{CO_2}$ concentration at x and t, respectively, M_{s} is the concentration of corrosive chemicals in the pore solution in concrete, $M_{\mathrm{i,ms}}$, $M_{\mathrm{s,ms}}$, and $M_{\mathrm{f,ms}}$ are the initial concentration of total molar in concrete, on the surface of the concrete structures, and at the interface between the concrete and rebar, respectively.

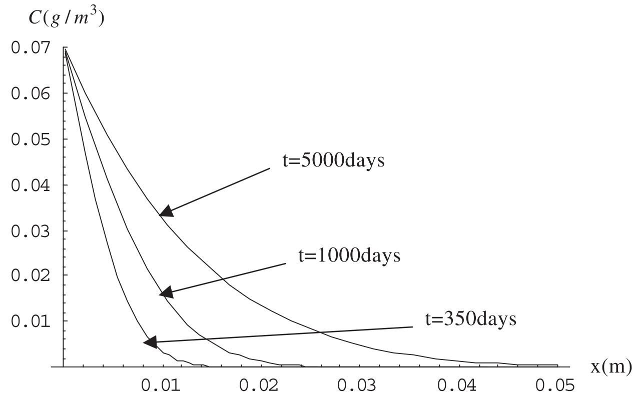

Fig. 11. Concentration–sulfation depth relationships under $R_{\mathrm{SO_4^{2-}}} = 0.8$.

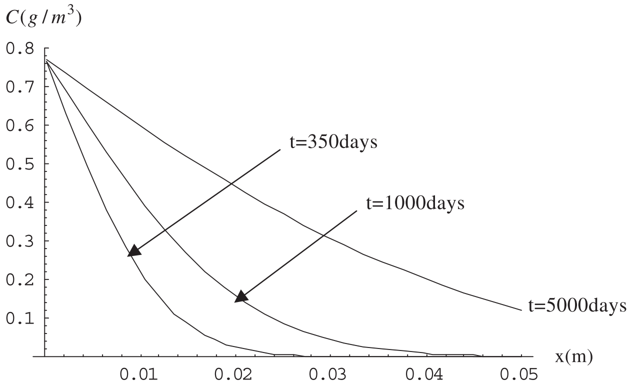

Fig. 12. Concentration–penetration depth of synergetic effect for $\mathrm{SO_4^{2-}}$ + $\mathrm{CO_2}$ under $R_{\mathrm{SO_4^{2-}}} = R_{\mathrm{CO_2}} = 0.8$.

Let $K_{T,\mathrm{Cl^-}} = KC_{\mathrm{CO_2}}$, $K_{T,\mathrm{CO_2}} = KC_{\mathrm{Cl^-}}$, and $K_{T,M_{\mathrm{s}}} = R_{\mathrm{C}}K' C_{\mathrm{Cl^-}}C_{\mathrm{CO_2}}$. Then, Eqs. (11)–(13) have the same analytical solutions as Eqs. (2) and (4), respectively.

If we consider the synergetic effect of sulfate and carbonate ions on reinforcing steel corrosion [15], we have a system of partial differential equations with initial and boundary conditions as follows:

$$\frac{\partial C_{\mathrm{SO_4^{2-}}}}{\partial t} = \frac{D_{\mathrm{s}}}{R_{\mathrm{SO_4^{2-}}}}\frac{\partial^2 C_{\mathrm{SO_4^{2-}}}}{\partial x^2} - \frac{\nu}{R_{\mathrm{SO_4^{2-}}}}\frac{\partial C_{\mathrm{SO_4^{2-}}}}{\partial x} - \frac{1}{R_{\mathrm{SO_4^{2-}}}} \times KC_{\mathrm{SO_4^{2-}}}C_{\mathrm{CO_2}} \tag{17}$$

$$\frac{\partial C_{\mathrm{CO_2}}}{\partial t} = D_{\mathrm{s}}\frac{\partial^2 C_{\mathrm{CO_2}}}{\partial x^2} - \nu\frac{\partial C_{\mathrm{CO_2}}}{\partial x} - KC_{\mathrm{SO_4^{2-}}}C_{\mathrm{CO_2}} \tag{18}$$

$$\frac{\partial M_{\mathrm{s}}}{\partial t} = \frac{D_{\mathrm{s}}}{R_{\mathrm{C}}}\frac{\partial^2 M_{\mathrm{s}}}{\partial x^2} - \frac{\nu}{R_{\mathrm{C}}}\frac{\partial M_{\mathrm{s}}}{\partial x} + M_{\mathrm{s}}K'C_{\mathrm{SO_4^{2-}}}C_{\mathrm{CO_2}} \tag{19}$$

$$C(x,0) = C_{\mathrm{i,SO_4^{2-}}} \quad C(x,0) = C_{\mathrm{i,CO_2}}$$

$$M_{\mathrm{s}}(x,0) = M_{\mathrm{i,ms}} \quad x > 0 \tag{20}$$

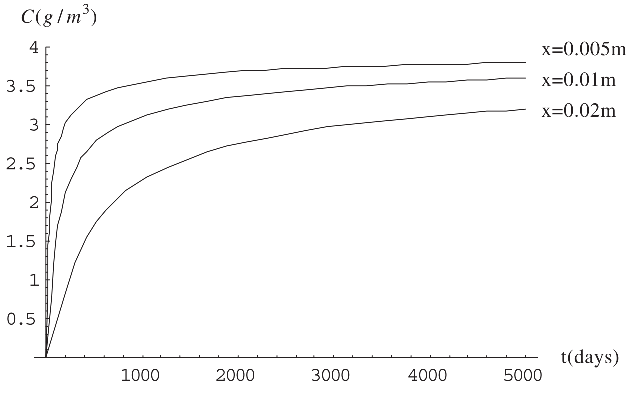

Fig. 13. Concentration–time relationships of $\mathrm{Cl^-}$ under $R_{\mathrm{Cl^-}} = 0.8$.

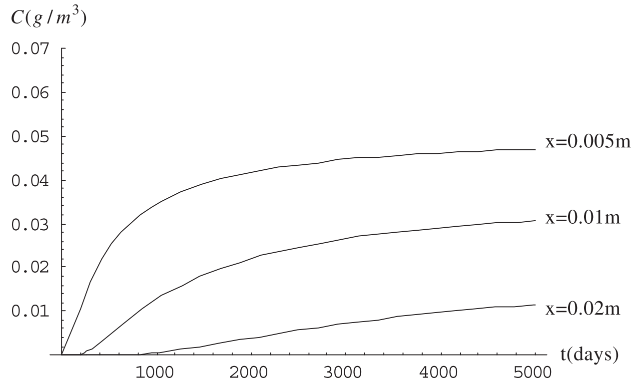

Fig. 14. Concentration–time relationships of SO_4^{2-}.

$$C(0,t) = C_{s,SO_4^{2-}} \quad C(0,t) = C_{s,CO_2}$$
$$M_s(0,t) = M_{s,ms} \quad t > 0 \tag{21}$$

$$C(L,t) = C_{f,SO_4^{2-}} \quad C(L,t) = C_{f,CO_2}$$
$$M_s(L,t) = M_{f,ms} \quad t > 0 \tag{22}$$

where $C_{SO_4^{2-}}$ is the SO_4^{2-} concentration at x and t, $C_{i,SO_4^{2-}}$, $C_{s,SO_4^{2-}}$, and $C_{f,SO_4^{2-}}$ are the initial concentration of SO_4^{2-} in concrete, the SO_4^{2-} concentration on the surface of the concrete structures, and the SO_4^{2-} concentration at the interface between the concrete and rebar, respectively.

If we evaluate the synergetic effect of sulfate on chloride diffusivity in concrete structures [19], we have a system of partial differential equations with initial and boundary conditions as follows:

$$\frac{\partial C_{Cl^-}}{\partial t} = \frac{D_s}{R_{Cl^-}}\frac{\partial^2 C_{Cl^-}}{\partial x^2} - \frac{\nu}{R_{Cl^-}}\frac{\partial C_{Cl^-}}{\partial x} - \frac{1}{R_{Cl^-}}K C_{Cl^-} C_{SO_4^{2-}} \tag{23}$$

$$\frac{\partial C_{SO_4^{2-}}}{\partial t} = D_s \frac{\partial^2 C_{SO_4^{2-}}}{\partial x^2} - \nu \frac{\partial C_{SO_4^{2-}}}{\partial x} - K C_{Cl^-} C_{SO_4^{2-}} \tag{24}$$

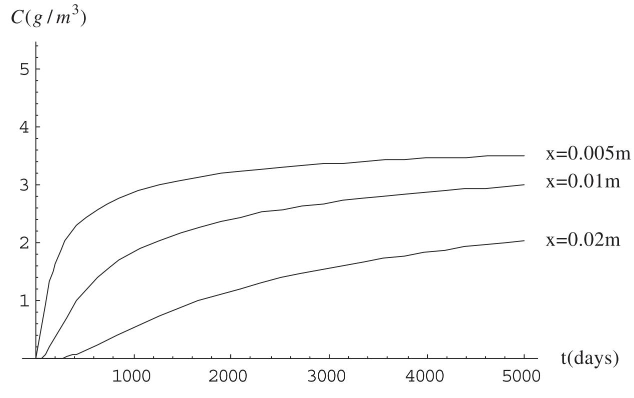

Fig. 15. Concentration–time relationships of synergetic effect for $Cl^- + SO_4^{2-}$ under $R_{Cl^-} = R_{SO_4^{2-}} = 0.8$.

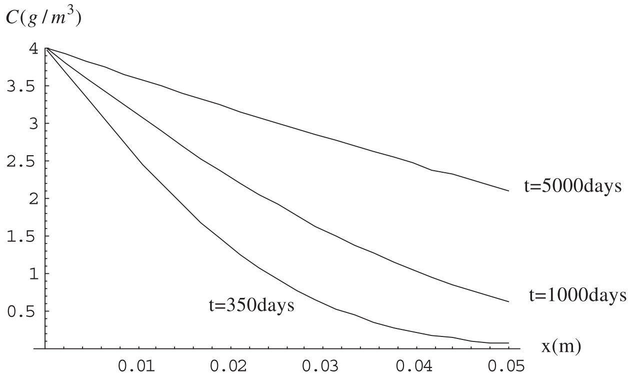

Fig. 16. Concentration–chlorination depth relationships under $R_{Cl^-} = 0.8$.

$$\frac{\partial M_s}{\partial t} = \frac{D_s}{R_C}\frac{\partial^2 M_s}{\partial x^2} - \frac{\nu}{R_C}\frac{\partial M_s}{\partial x} + M_s K' C_{Cl^-} C_{SO_4^{2-}} \tag{25}$$

$$C(x,0) = C_{i,Cl^-} \quad C(x,0) = C_{i,SO_4^{2-}}$$
$$M_s(x,0) = M_{i,ms} \quad x > 0 \tag{26}$$

$$C(0,t) = C_{s,Cl^-} \quad C(0,t) = C_{s,SO_4^{2-}}$$
$$M_s(0,t) = M_{s,ms} \quad t > 0 \tag{27}$$

$$C(L,t) = C_{f,Cl^-} \quad C(L,t) = C_{f,SO_4^{2-}}$$
$$M_s(L,t) = M_{f,ms} \quad t > 0 \tag{28}$$

For the synergetic effect of both sulfate and carbonate ions and sulfate on chloride diffusivity, the analytical solution can be obtained according to the method of synergetic effect between Cl^- and CO_2 mentioned above.

3. Numerical results

The computer package "Mathematica" [22] was used to show the synergetic effect of multiple corrosive chemicals in concrete structures.

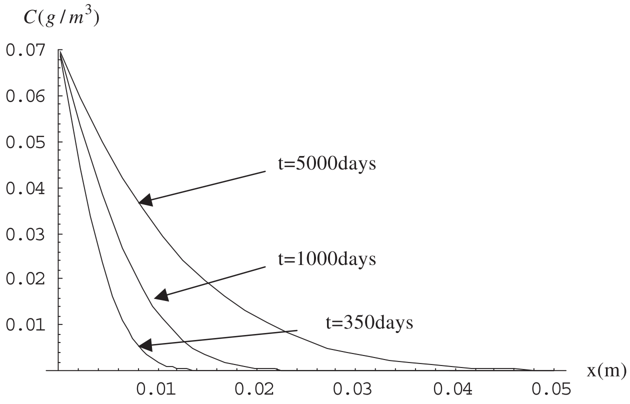

Fig. 17. Concentration–sulfation depth relationships.

If $C_{CO_2} = 0.3$ g/m^3, $C_{Cl^-} = 1.6$ g/m^3, $K = 5 \times 10^{-10}$ m^3/g s, $K_{T,Cl^-} = 1.5 \times 10^{-10}$ 1/s, $D_{s,Cl^-} = 5 \times 10^{-12}$ m^2/s, $\nu = 10^{-12}$ m/s, $C_{i,Cl^-} = 0$ g/m^3, $C_{s,Cl^-} = 4$ g/m^3, $C_{f,Cl^-} = 0$ g/m^3 $K_{T,CO_2} = 8 \times 10^{-10}$ 1/s, $D_{s,CO_2} = 10^{-11}$ m^2/s, C_{i,CO_2}, 0 g/m^3, $C_{s,CO_2} = 0.7$ g/m^3, $C_{f,CO_2} = 0$ g/m^3, $K_{T,M_s} = 2.4 \times 10^{-10}$ 1/s, $D_{s,ms} = 7 \times 10^{-12}$ m^2/s, $K' = 5 \times 10^{-10}$ m^6/g^2 s, and $M_{s,ms} = 4.7$ g/m^3 are given, then we have the synergetic effect between Cl^- and CO_2, represented by the concentration–time relationships and concentration–corrosive chemical penetration depth relationships obtained from Eqs. (11)–(16), as shown in Figs. 1–6. From these figures, it is very obvious that the corrosion depth of synergetic effect is larger than that of single attack, only CO_2 or Cl^-. If $C_{CO_2} = 0.3$ g/m^3, $C_{SO_4^{2-}} = 0.02$ g/m^3, $K = 5 \times 10^{-9}$ m^3/g s, $K' = 5 \times 10^{-9}$ m^6/g^2 s, $K_{T,SO_4^{2-}} = 1.5 \times 10^{-9}$ 1/s, $K_{T,CO_2} = 10^{-10}$ 1/s, $K_{T,M_s} = 3 \times 10^{-11}$ 1/s, $\nu = 10^{-12}$ m/s, $D_{s,SO_4^{2-}} = 3 \times 10^{-13}$ m^2/s, $D_{s,CO_2} = 10^{-11}$ m^2/s, $D_{s,ms} = 10^{-12}$ m^2/s, $C_{i,SO_4^{2-}} = 0$ g/m^3, $C_{s,SO_4^{2-}} = 0.07$ g/m^3, $C_{f,SO_4^{2-}} = 0$ g/m^3, C_{s,CO_2}=0 g/m^3, C_{s,CO_2}=0.7 g/m^3, C_{f,CO_2}=0 g/m^3, and $M_{s,ms}$=0.77 g/m^3$C_{f,CO_2} = 0$ g/m^3, and $M_{s,ms} = 0.77$ g/m^3 are known, then we find the synergetic effect between SO_4^{2-} and CO_2 presented by the concentration–time relationships and the concentration–corrosive chemical penetration depth relationships obtained from Eqs. (17)–(22), as denoted in Figs. 7–12. It is clearly seen from these figures that the accelerated corrosion due to synergetic effect is extremely evident. If $C_{SO_4^{2-}} = 0.02$ g/m^3, $C_{Cl^-} = 1.6$ g/m^3, $K = 10^{-9}$ m^3/g s, $K' = 10^{-9}$ m^6/g s, $K_{T,SO_4^{2-}} = 1.6 \times 10^{-9}$ 1/s, $K_{T,Cl}{}^- = 2 \times 10^{-11}$ 1/s, $K_{T,Ms}$=3.2 × 10^{-11} 1/s, $\nu = 10^{-12}$ m/s, $D_{s,SO_4^{2-}} = 3 \times 10^{-13}$ m^2/s, $D_{s,Cl^-} = 5 \times 10^{-12}$ m^2/s, $D_{s,ms} = 7 \times 10^{-13}$ m^2/s, $C_{i,SO_4^{2-}}$ =0 g/m^3, $C_{s,SO_4^{2-}} = 0.07$ g/m^3, $C_{f,SO_4^{2-}} = 0$ g/m^3, $C_{i,Cl^-} = 0$ g/m^3, $C_{s,Cl^-} = 4$ g/m^3, $C_{f,Cl^-} = 0$ g/m^3, and $M_{s,ms} = 4.07$ g/m^3 are supplied, then we have the synergetic effect between Cl^- and SO_4^{2-} described by the concentration–time relationships and the concentration–corrosive chemical penetration depth relationships gained from Eqs. (23)–(28), as indicated in Figs. 13–18. From these figures, it is not to be doubted that the corrosion depth of synergetic effect is larger than that of single attack, only SO_4^{2-} or Cl^-.

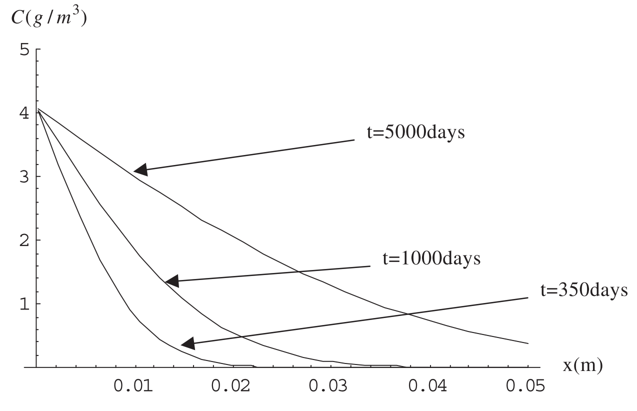

Fig. 18. Concentration–penetration depth of synergetic effect for $Cl^- + SO_4^{2-}$ under $R_{Cl^-} = R_{SO_4^{2-}} = 0.8$.

4. Discussion

The system of a set of partial differential equations such as Eqs. (11)–(22) and Eqs. (23)–(28) were provided as a synergetic effect study for concrete structures passed through binary contamination ingress. Each equation of the system is a one-dimensional linear diffusion equation, which is attributed to the equation of continuity. To obtain the suitable parameters for the numerical solution, the simplest experiment of single attack, only chloride, CO_2, or sulfate ions, is first indispensable to treat for concentration, C, and diffusion coefficient, D. Second, according to the equation of continuity, the other parameters, such as K_T, K', and M_s, are evaluated from the experimental results of the $C-t$ curve [23]. Third, the value of ν is a function of water–cement ratio and concentration gradient. Based on the principle of conservation of mass, the experimental result with synergetic effect can also be calibrated each parameter.

Now consider the one-dimensional diffusion equation with initial and boundary conditions.

$$\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial x^2} \tag{29a}$$

$$C(x,0) = C_i = 0 \tag{29b}$$

$$C(0,t) = C_s = C_0, \; C(L,t) = C_f = 0 \tag{29c}$$

Taking the Laplace transform method, the analytical solution for Eqs. (29a)–(29c) is

$$C(x,t) = C_0 \operatorname{erfc}\left(\frac{x}{\sqrt{4D_s t}}\right) \tag{30}$$

where erfc(·) is the complementary error function. Eq. (30) is usually called Fick's second law.

Eq. (30) may be written as

$$x(t) = A\sqrt{t} \tag{31}$$

where $A = \sqrt{4D_s}\operatorname{erfc}^{-1}(C/C_0)$ is constant, $x(t)$ is the corrosive chemicals penetration front, and t is the time.

Tumidajski and Chan [19] used Eq. (31) to present the synergistic effect of sulfate ion on chloride ingress into the Portland cement concrete and concrete incorporating partial replacement of Portland cement by slag. This is obviously oversimplified and completely unreasonable. Because Eq. (31) is the analytical solution of Eqs. (29a)–(29c), Eqs. (29a)–(29c) only considers the diffusion item. However, when we explore the synergetic effect of multiple corrosive chemicals in concrete structures, the mechanical driving force, due to the reduction of corrosive chemical concentration, plays an important role. It is worthy to point out that the proposed model is very suitable to elucidate the synergetic effect of two corrosive chemicals in concrete structures.

The equations of change for a synergetic effect of multiple corrosive chemicals are given in terms of the mass flux. To obtain expressions for the profiles, we have to be able to replace the mass flux by an expression that contains the transport property and the concentration gradient. This means that the equation of continuity was rewritten by inserting an expression for the mass flux in terms of the concentration gradient. Actually, the most important contribution to the mass flux is that resulting from the concentration gradient. It is known, however, that even in an isothermal system there are certainly three mechanical driving forces that tend to produce the movement of a corrosive chemical species with respect to the mean fluid motion in porosity of concrete: (a) the concentration gradient, (b) the pressure gradient, and (c) external forces acting unequally on the various corrosive chemical species. In this article, the second and third of these mechanical driving forces have been neglected to simplify the highly complex problem of the synergetic effect.

5. Conclusions

A new concept of the transport phenomena of chloride, CO_2, and sulfate ions in concrete structures, using a set of one-dimensional linear diffusion equations, has been represented. The analytical solution for the one-dimensional linear diffusion equation can be solved by using the method of Laplace transform associated with the substitution method and the convolution theorem. By treating a transport phenomenon as a concrete structure corrosive chemical process, this new mathematical model can be used to describe more accurately the synergetic effect than the currently used simple formula such as Fick's second law. As to modeling the synergetic effect of a concrete structure corrosive chemical process, the evaluated corrosion results obtained from the diffusion equations for a binary mixture is larger than those of the results obtained from the single corrosive media attack. However, it is recommended that experiments should be performed for selecting suitable parameters for the numerical simulation. Both the experimental and numerical results should also be compared.

Acknowledgements

The authors would like to thank the National Science Council of the ROC for its financial support of this study under contract NSC 89-2211-E-019-030.

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