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Sulfate Diffusion in Concrete

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ABSTRACT

The sulfate diffusion coefficient is a variable in theoretical models used for predicting the service life of concrete. Analysis of sulfate models predicts that if the process is either diffusion or reaction controlled, a 10-fold increase in the diffusion coefficient results in a 10-fold increase in the predicted service life. Therefore, reliable estimates of sulfate diffusion coefficients are needed to make reasonable service life predictions.

Methods for determining the sulfate diffusion coefficient of sulfates in cement-based materials are explored in this paper, including experimental methods and mathematical modeling. Also, an approach for estimating the diffusion coefficient of sulfate ions is presented, which is based on comparing sulfate diffusion coefficients with chloride diffusion coefficients.

Key words: building technology; concrete; diffusion coefficient; radioactive waste; service life; sulfate attack

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1. INTRODUCTION

Sulfate attack is one of the possible major degradation processes for concrete vaults buried underground for the disposal of low-level radioactive waste (LLW) [1]. The diffusion coefficient for sulfates in the pore water of concrete is a variable in most models for predicting the service life of concrete controlled by sulfate attack [2,3]. These service life predictions are sensitive to the values of the sulfate diffusion coefficient [3]. Because of the lack of data on sulfate diffusion coefficients, the diffusion coefficient for chloride ions in cement paste has been used as the value of the sulfate diffusion coefficient in making service life predictions [3]. Therefore, information is needed on values of sulfate diffusion coefficient to make reasonable service life predictions when sulfate is the controlling degradation process. Methods for determining the sulfate diffusion coefficient in cement-based materials are explored in this paper, including experimental methods and mathematical modeling. Also, a method for estimating the diffusion coefficient of sulfate ions is presented, which is based on comparing sulfate diffusion coefficients with chloride diffusion coefficients.

We are using intrinsic diffusion coefficient, D_i, to denote the diffusion coefficient in a porous medium without absorption or reaction occurring, while effective diffusion coefficient, D_e, denotes the diffusion coefficient in a porous medium in which either or both absorption and reaction occurs.

2. EXPERIMENTAL METHODS FOR OBTAINING SULFATE DIFFUSION COEFFICIENTS

2.1 Determination of Sulfate Diffusion Coefficient Using Diffusion Cells.

Using a conventional diffusion cell, similar to that described by Clifton, et al. [4], for measuring the diffusion coefficient of sulfate ions through cement-based materials is significantly more difficult using it for measuring chloride ion diffusion coefficients. For example, the concentration (activity) of chloride ions which have diffused through a specimen can be monitored with an ion selective electrode. However, an ion selective electrode is not available for sulfate ions. The concentration of sulfate can be measured by several other methods including precipitating the sulfate as barium sulfate and gravimetrically determining the sulfate content [5]; by potentiometric titration using a lead salt [6]; or by a turbidimetric method described by Atkinson, et al. [7]. These methods are significantly more time consuming than direct measurements using a selective ion electrode.

Calcium sulfate, usually in the form of gypsum, is blended with clinker during grinding. This calcium sulfate is added to reduce the initial high rate of rapid hydration of tricalcium aluminate and prevent flash set caused by [8]. Thus, some of the sulfate accumulating in the diffusion cell would be internal sulfate and, thus, would increase the measured or effective diffusion coefficient. Another complication in measuring sulfate diffusivity using a diffusion cell is the possible degradation of specimens caused by sulfate reactions with constituents of the cement. For example, diffusing sulfate ions could react with tricalcium aluminate hydration products to form ettringite. Ettringite occupies more volume than the solid reactants, therefore, its formation could result in cracking of specimens.

2.2 Determination of Sulfate Diffusion Coefficient by Radioactive Tracers

A radioactive traced method was developed by Spinks, et al. [9] for studying the diffusion process of anions and cations in hardened portland cement paste. They labeled salts with ^{45}Ca, ^{35}S, ^{121}I, and ^{22}Na, and exposed cement and mortar specimens to aqueous solutions of the labeled salts. The depth of diffusion of salts was measured by cutting slices from the specimens and measuring the radioactivity of the slices with a Geiger counter. Effective diffusion coefficients were calculated using Fick's first law of diffusion. For a 1:2 mortar (one part by mass of cement to 2 parts by mass of Ottawa sand), D_e for sulfate was 6.1×10^{-14} m^2/s, and for iodine it was 130×10^{-14} m^2/s, giving a ratio for the diffusivity of iodide ions to sulfate ions of 21. Since the chloride diffusion coefficient for cement paste is essentially identical to that of iodide diffusion [10] the ratio of the effective chloride diffusion coefficient (D_{eC}) to sulfate diffusion coefficient (D_{eS}) also should be close to 21.

Unfortunately, the water to cement ratios (w/c) of the cement paste and mortar were not reported. Since no water-reducers were reported to be added, it is likely that the w/c ratios were above 0.4.

A major benefit of the radioactive tracer method for measuring the depth of penetration of sulfate into cement-based materials is that the calcium sulfate added as a set-regulator to portland cements is not radioactive and thus will not be detected.

2.3 Determination of Sulfate and Chloride Penetration Profiles by EDXA.

Penetration profiles of chloride and sulfate ions into concrete were studied by Feldman, et al.[11] by using energy dispersive X-ray analysis (EDXA). Concretes were made from two portland cements, Canadian Types 10 and 50, respectively equivalent to ASTM Type I and Type V portland cements, and slag and silica fume

mineral admixtures. Data were reported for one year of diffusion studies. Depth of penetration was taken to be the depth at which the concentration of diffusing sulfate or chloride ions became equal to the intrinsic concentrations of the concrete, based on chemical analysis.

Four w/c ratios, 0.35, 0.42, 0.5, and 0.60 were used, and denoted as mixes M1, M2, M3,and M4, respectively. Three concrete systems, S1, S2, and S5, were made at each w/c ratio as follows: S1 - Type 10 portland cement; S2 - 90% Type 50 portland cement + 10% silica fume; S5 - 75% blast furnace slag + 22% Type 50 portland cement + 3% silica fume.

Data were available in tabular and graphic form for the depth of ingress of sulfate and chloride ions at specific times. The conventual method of analyzing such data is to use the classical error function solution [12]:

$$\frac{C - C_b}{C_s - C_b} = erfc \frac{x}{(4D_e t)^{1/2}} \tag{1}$$

Where C_s is the surface concentration of either chloride or sulfate ion,

C_b is the background (or initial) concentration of either chloride or sulfate
C is the concentration at a specific depth and time,

x is the depth where the concentration of diffusing ions is 0, i.e., $C = C_b$,

D_e is the effective diffusion coefficient, and

t is time.

Another approach to calculation D_e without the use of the error function has been provided by Bazant [13]. The advantage of this method is that the calculation of D_e can be easily computerized. He derived the following parabolic equation:

$$\frac{C - C_b}{C_s - C_b} = [1 - (1/3^{1/2} \cdot x/2D_e t)^{1/2}]^2 \tag{2}$$

Solutions for eq. (2) are consistent with those for eq. (1) over the range of the dimensionless variable $x/2(D_e t)^{1/2}$ from 0 to $3^{1/2}$, differing in this range by no more than 0.033.

Setting the concentration C equal to the background concentration C_b in eq. (2) and rearranging:

$$D_e = x^2/12t \tag{3}$$

The method used here is consistent with the method of dimensionless groups given by Pommersheim and Clifton [14]. Eq. (3) predicts a dimensionless time ratio of $tD_e/x^2 = 1/12$. Since this ratio is much less than unity, the conditions are far from steady state. It is thus appropriate to use eq. (3) to obtain approximations of the effective diffusivities of ions in concrete or cement paste.

Using eq. (3) the diffusion coefficients were calculated for the three batches and four mixes, and the results are given in Table 1. The results are consistent with those reported by Spinks, et al [7], since in all cases the individual chloride ion diffusion coefficients were higher than those for sulfate. The ratio D_{eC}/D_{eS} was 10 or higher except for the w/c of 0.6 with the S5 concrete system. It should be noted that the cement mixture in S5 largely consisted of blast furnace slag, while systems S1 and S2 were mostly portland cement (S2 contained 10% silica fume).

3. MODELING OF SULFATE DIFFUSION

Two approaches for modeling sulfate diffusion are described: a finite difference model; and a "blind ant model." These approaches are both being used in modeling studies at the National Institute of Standards and Technology on transport properties.

3.1 Finite Difference Model for Sulfate Diffusion/Reaction

This approach used a one-dimensional model for the ingress of sulfate ions from a constant concentration source into a slab of hardened cement paste. The cement paste is initially free of unbound sulfate ions (C=0). The sulfate ions diffuse into the cement and are consumed in an irreversible reaction with calcium hydroxide acording to:

$$SO_4^{2-} + Ca(OH)_2 \rightarrow CaSO_4 + 2OH^- \tag{4}$$

Table 1. Ratio of Chloride Diffusivity to Sulfate Diffusivity*

Concrete System: S1

w/c:	0.35	0.42	0.50	0.60
D_{eC} (m^2/s)	$4.8x10^{-13}$	$6.6x10^{-13}$	$1.9x10^{-12}$	$3.6x10^{-12}$
D_{eS} (m^2/s)	$4.9x10^{-14}$	$4.0x10^{-14}$	$1.3x10^{-13}$	$0.98x10^{-13}$
Ratio D_{eC}/D_{eS}	10	16	15	27

Concrete System: S2

w/c:	0.35	0.42	0.50	0.60
D_{eC} (m^2/s)	$2.9x10^{-13}$	$3.4x10^{-13}$	$4.9x10^{-13}$	$1.6x10^{-13}$
D_{eS} (m^2/s)	$1.9x10^{-14}$	$2.2x10^{-14}$	$1.7x10^{-14}$	$1.7x10^{-14}$
Ratio D_{eC}/D_{eS}	15	14	29	39

Concrete System: S5

w/c:	0.35	0.42	0.50	0.60
D_{eC} (m^2/s)	$4.2x10^{-14}$	$1.9x10^{-14}$	$4.4x10^{-14}$	$1.1x10^{-13}$
D_{eS} (m^2/s)	$2.7x10^{-15}$	$1.7x10^{-15}$	$4.5x10^{-15}$	$2.1x10^{-14}$
Ratio D_{eC}/D_{eS}	16	11	10	5.2

*Based on penetration data from reference no.11.

According to Crank [12], the standard differential equation for this problem is:

$$\frac{\partial C}{\partial t} = D_i \frac{\partial^2 C}{\partial x^2} - kC \tag{5}$$

where C is the concentration of sulfate ions at time t and position x, D_i is the intrinsic diffusion coefficient (m^2/s) and k is the reaction rate constant (s^{-1}). The development assumes that sulfate is consumed by a first order chemical reaction and that transport occurs only in the x direction, i.e., one-dimensional diffusion. It also assumes that the concentration of sulfate ions controls reaction (4) above since the concentration of calcium hydroxide does not appear in eq. (5). The solution to eq. (5) for this system is also given by Crank [12]:

$$\begin{aligned}\frac{C}{C_0} &= \frac{1}{2}\exp\left(-x\sqrt{\frac{k}{D_i}}\right) erfc\left(\frac{x}{2\sqrt{D_i t}}-\sqrt{kt}\right)\\ &+\frac{1}{2}\exp\left(x\sqrt{\frac{k}{D_i}}\right) erfc\left(\frac{x}{2\sqrt{D_i t}}+\sqrt{kt}\right)\end{aligned} \tag{6}$$

Eq. (6) could be plotted to provide concentration vs. position for any given time t. The difficulty arises in that an infinite supply of calcium hydroxide does not exist in the cement paste so that at each position in the sample of interest, reaction (4) will terminate at some specific time.

Since this constraint cannot be conveniently handled analytically, a finite difference method is applied to this problem. The spatial and temporal derivatives in eq.(6) are approximated by:

$$\begin{gathered}\left(\frac{\partial^2 C}{\partial x^2}\right)_m = \left(\frac{C_{m+1}-2C_m+C_{m-1}}{(\Delta x)^2}\right)\\ \left(\frac{\partial C}{\partial t}\right)_m = \frac{C_m^+-C_m}{\Delta t}\end{gathered} \tag{7}$$

where subscripts indicate spatial locations and superscripts indicate points in time respectively. Δx and Δt indicate the step sizes in space and time for the finite difference method. The equations in (7) can be substituted into eq. (5) and giving an iterative solution for the new concentration at location m:

$$C_m^+ = C_m + \Delta t\left[\frac{D_i}{(\Delta x)^2}(C_{m+1}-2C_m+C_{m-1}) - kC_mR_m\right] \tag{8}$$

where R_m is a flag (with values of 0 or 1) indicating if reaction can occur at position m. R_m is set equal to 0 when all of the calcium hydroxide is consumed at a given depth m. At the far end

(zero flux) boundary condition is used so that eq.(8) becomes [14]:

$$C_m^+ = C_m + \Delta t\left[\frac{D_i}{(\Delta x^2)}(2C_{m-1}-2C_m) - kC_mR_m\right] \tag{9}$$

Eqs. (8) and (9) can be solved using the computer to give sulfate concentration as a function of time and position. An initial study was conducted with the following parameters:

Surface concentration-	1.0 moles/liter
Volume of a layer-	0.01 liters
Thickness of a layer (Δx)-	0.001 meters
Diffusion coefficient (D_i)-	$1*10^{-12}$ m^2/s
Reaction constant (k)-	$0, 1*10^{-6}, 1*10^{-8}$ s^{-1}
CH volume fraction-	0.22
Time step (Δt)-	$1*10^5$ seconds
Total number of steps-	50000 or $5*10^9$ seconds

The calcium hydroxide volume fraction of 0.22 would be typical for a fully hydrated cement paste with a w/c ratio in the range of 0.4 to 0.5 [15].

The results are shown in Fig. 1 for times of $1x10^8$, $5x10^8$, and $5x10^9$ seconds, corresponding to about 3.2, 15.9, and 159 years respectively. The effects of reaction on impeding the penetration of sulfate ions into the cement paste are evident from the plots in Fig. 1. The value of the reaction constant k had a significant effect on the progress of sulfate penetration. Thus, this parameter and the diffusion coefficient D_i must be known to predict the penetration of sulfate ions into a cement paste or concrete specimen.

3.2 Blind Ant Model for Sulfate Diffusion in Cement Paste

An alternate approach for simulating diffusion/reaction processes in a random porous media is the utilization of random walkers as described in detail in [16]. This approach was first applied to diffusion problems in the early 1950s [17]. Here, walkers (commonly known as blind ants) are released at random locations in the pore space of a porous media. The walkers undergo random Brownian motion-type diffusion with the restriction that they cannot enter the solid phase of the porous media. When a step would land a walker in the solid phase, the step is not allowed, but the timer still advances. By monitoring the average distance a walker travels over time, a diffusion coefficient for the porous media can be determined [18].

This basic approach was modified to study the diffusion/reaction of sulfate ions in cement paste. First, instead of releasing random walkers throughout the pore space, a constant concentration of walkers was maintained at one surface of the porous media to simulate the experimental boundary condition. Second, the walkers were allowed to diffuse freely in both the capillary pore space and the nanoporous calcium silicate hydrate (C-S-H) gel phase. Finally, as the walkers are diffusing, they may be consumed in a reaction at the surface of a calcium hydroxide crystal according to the stoichiometry given in equation (4).

This approach has been used previously to study the diffusion/binding of chloride ions in hardened cement paste [18]. To do this, the cement paste microstructure is represented in the computer as a two-dimensional array of elements (called pixels). Each element is uniquely identified as one of the phases of cement paste; in its simplest form the phases to be considered are capillary porosity, unreacted cement, C-S-H gel, and calcium hydroxide. This two-dimensional representation could be obtained from a scanning electron microscope image of a real hydrated sample or from a digital-image-based computer simulation [19]. Fig. 2 shows a 250x1000 digital image created using the NIST cement hydration microstructural model [18,19]. Each element is about 1 μm^2 in size so that the sample shown in Fig. 2 would be 0.25 by 1.0 mm. White indicates calcium hydroxide, light grey is unreacted cement, dark grey is C-S-H gel, and black is porosity. The original system, having a w/c ratio of 0.5, was created from a data-base of real cement particle shapes obtained by a combination of scanning electron microscopy and image analysis [20]. In the hydrated image shown in Fig. 2, a degree of hydration of 0.87 was achieved using the microstructural model.

This image can be used as input into a computer simulation for the diffusion/reaction of sulfate ions in cement paste. As outlined previously, the sulfate ions are represented by random walkers which can diffuse from pixel to pixel within the porosity and C-S-H gel phases and react with the solid calcium hydroxide, forming calcium sulfate, according to eq. (4). By initially placing and subsequently maintaining a constant number of random walkers at the top surface of the system, diffusion under a concentration gradient can be simulated. The reaction rate of calcium hydroxide with the sulfate ions can be controlled by designating a probability of reaction when a diffusing sulfate species "collides" with a solid calcium hydroxide pixel. By specifying this probability to be zero, the no reaction case can be simulated as a control system. By tabulating how many sulfate species are consumed by each pixel of calcium hydroxide, the local reaction can terminated when all of the solid calcium hydroxide at a specific pixel has been depleted according to the stoichiometry in the reaction of eq. (4). As in the finite difference solution, the concentration of sulfate species as a

function of depth can be monitored throughout the simulation to produce the concentration vs. distance curves counterpart to those in Fig. 1.

Since each sulfate walker can represent a collection of diffusing ions, the simulation was executed such that one walker per pixel corresponded to a concentration of 0.1 M. Maintaining 2500 walker along the top surface of the microstructure results in a surface concentration of 1 M. Results for this simulation are shown in Fig. 3 for three different reaction probabilities (k) after 200000 steps have been taken. The form of the results is seen to closely follow that of those shown in Fig. 1, validating that the "blind ant" method can produce results equivalent to the finite-difference approach. The advantage of the blind ant method is that it can be applied to a specific heterogeneous cement paste microstructure (real or simulated), whereas the finite difference approach considers the microstructure to be homogeneous or, at most, to consist of a series of homogeneous layers.

Both techniques clearly illustrate that reaction can significantly slow the ingress of sulfate ions into a cement paste specimen. To quantify this effect, the kinetics of the reactions occurring must be measured either directly or indirectly. As Fig. 1 shows, the kinetics could be inferred by monitoring the advance of a "sulfate front" into a specimen over time. The methods described in section 2 could be used to monitor the movement of a sulfate front or, if not present, to monitor the maximum depth of ingress of sulfate ions as a function of time.

The simulation models described in this paper should be further developed to provide a means of extending experimental studies on the diffusivity of both chloride and sulfate ions in concrete to other concrete mixtures and exposure conditions. Sulfate diffusion studies are especially difficult to carry out and with further development it is reasonable to expect that modeling should provide a means for estimating sulfate diffusion coefficients.

4. DISCUSSION

4.1 Comparison of Diffusivity of Chloride and Sulfate Ions

The diffusion coefficient of chloride ions and sulfate ions at infinite dilution in bulk water (free stream values) are 2.03×10^{-9} and 1.07×10^{-9} m^2/s, respectively [21]. These values are some three to five orders of magnitude larger than the diffusivities in cement-based materials because:

(1) the effective area of diffusion is lowered by the

presence of the solid phase.

(2) the connectivity of the pores may not be continuous

(3) the diffusion path is tortuous which increases the path length

(4) a given diffusion path has constricted regions which give a greater resistance to the diffusive flow of molecules or ions.

The effects of these constraining factors are mathematically expressed in the relationship [22]:

$$D_{iA}=D_A\epsilon\frac{\sigma}{\tau} \tag{11}$$

The porosity ϵ (volume fraction pores) and constriction factor σ are both less than unity, while the tortuosity factor τ is greater than unity. These factors act to lower the intrinsic diffusion coefficient, D_{iA}, of species A relative to its free stream value D_A. Because the geometrical factors, σ and τ are complex functions of pore structure, it is not, at present, feasible to use eq. (11) for reliable calculations of D_{eA}. Another factor which can reduce the intrinsic diffusion coefficient which is not often considered, is the effect of concentration. Increasing the concentration of diffusing ions will tend to decrease D_i [12].

The diffusion coefficient of chloride and sulfate ions diffusing through the same cement-based materials will both be equally effected by the above physical factors. Thus, the ratios of the intrinsic diffusion coefficients, D_{iC}/D_{iS}, should be approximately 2. However, this analysis does not consider the effects of binding by reaction and absorption processes. The ratios for effective diffusion coefficients, D_{eC}/D_{eS}, given in section 2, indicate that sulfate diffusion is significantly more strongly affected by binding than chloride ions. Chloride ions are known to react with the hydration products of tricalcium aluminate and the ferrite phase ($4CaO-Al_2O_3-FeO$) in hydrated cement to form Friedel's salt ($3CaO-Al_2O_3-CaCl_2-10H_2O$) [23]; whereas, sulfate ions penetrating into concrete are likely to be bound by reaction with calcium hydroxide, tricalcium aluminate hydration products such as monosulfate ($3CaO-Al_2O_3-CaSO_4-12H_2O$), and unreacted tricalcium aluminate [24]. Because there is more calcium hydroxide present in hydrated portland cement than aluminates, it is reasonable to assume that the effective diffusion coefficient of sulfate ions would be less than that of chloride ions. In making this analysis, it is recognized that the binding capacity of a concrete for chloride and sulfate ions may be dependent on the its mix proportions and constituents, especially

if mineral admixtures are added.

4.2 Predicting the Diffusion Coefficient for Sulfate Ions

An approach for estimating the diffusion coefficient of sulfate ions in concrete is demonstrated in the following. The diffusion coefficient of chlorides as a function of the w/c ratio of concrete can be calculated using equations such as [25]:

$$D_{Cl}(m^2/s) = 3.17x10^{-14}[2460(w/c - 0.30)^2 + 15] \qquad \textbf{(12)}$$

Based on the analysis in Table 1 and the study by Spinks, et al. [9], a conservative value of 0.10 is used for the ratio of D_{eS}/D_{eC}. Introducing this ratio into eq. (12), the equation for sulfate diffusion coefficient becomes:

$$D_{SO4}(m^2/s) = 3.17x10^{-15}[2460(w/c - 0.30)^2 + 15] \qquad \textbf{(13)}$$

For example if the w/c ratio is 0.4, then the predicted sulfate diffusion coefficient is $1.3x10^{-13}$ m^2/s. Note that eqs. (12) and (13) are not valid if w/c < 0.3, otherwise they would predict that the effective diffusion coefficient would increase as w/c decreases below 0.30.

The relationship between D_{Cl} and w/c in eq. (12) was used for demonstration purposes. Other equations have been reported [26] for calculating chloride ion diffusion coefficients as a function of w/c ratios that are equally credible as is eq. (12). They can be modified, as described above, to estimate diffusion coefficients for sulfate ions intruding concrete.

4.3 Effect of Sulfate Diffusion Coefficient Values on Service Life Predictions

Two different types of models have been developed for making predictions of service life when the controlling degradation process is sulfate attack: 1) a shrinking core model, and a 2) reaction controlled model (or mechanistic model).

In the shrinking core model [27], which is diffusion controlled, sulfate ions move through degraded concrete to the interface of unreacted concrete, and then rapidly reacts with the hydration products of tricalcium aluminate to form expansive products such as ettringite. Mass transport equations are used, assuming a quasi-steady state, to predict the movement of sulfate within the concrete. The flux of sulfate ions, N, is given by:

$$N = D_e(C_o/x) \quad (14)$$

where C_o is the concentration of sulfate in the bulk solution, D_e is the effective diffusion coefficient, and x is the depth of attack.

The rate of attack, dx/dt, is given by the rate of mass transport divided by the concentration of solid tricalcium aluminate, C_a:

$$dx/dt = -N/C_o = D_eC_o/C_ax \quad (15)$$

Integrating eq. (15) gives:

$$x^2 = 2D_e\frac{C_o}{C_a}t \quad (16)$$

If x is the depth of sulfate attack which results in unacceptable performance of a concrete element or structure, then according to eq. (16), a ten-fold increase in D_e will decrease the service life by 10.

In the reaction controlled model [3], it is assumed that:

(1) sulfate ions from the environment penetrate the concrete, by diffusion,
(2) sulfate ions react expansively with aluminates in the concrete, and
(3) cracking and delamination of concrete surfaces result from the expansive reactions.

Cracking and delamination of the concrete surface exposes a new surface to a concentration of sulfate ions near that of the groundwater sulfate concentration, rather than the smaller concentration resulting from diffusion. The model predicts that rate of sulfate attack will be largely controlled by the concentration of sulfate ions and aluminates, diffusion and reaction rates, and the fracture energy of concrete. The degradation rate (R) is linear in time (m/s) and is given by [3}:

$$R = X_{spall/Tspall} = (EB^2c_sC_{oe}D_i)/(\alpha\gamma\ (1-v) \quad (17)$$

where X_{spall} is the thickness of a spalled layer,
T_{spall} is the time for a layer to spall,
E is Young's modulus,
B is the linear strain caused by one mole of sulfate,

reacted in 1 m^3 of concrete,
c_s is the sulfate concentration in bulk solution,
C_{oe} is the concentration of reacted sulfate as ettringite,
D_i is the intrinsic diffusion coefficient of sulfate ions,
α_o is a roughness factor for fracture path (assumed to be 1.0),
γ is the fracture surface energy of concrete, and
v is Poission's ratio.

Note that both the shrinking core model and the reaction controlled model predict that a 10-fold increase in the diffusion coefficient of sulfate will result in a 10-fold decrease in service life. Therefore, representative estimates of sulfate diffusion coefficients are needed to make reasonable service life predictions.

5. SUMMARY AND CONCLUSIONS

The sulfate diffusion coefficient is a variable in theoretical models used for predicting the service life of concrete. Models based on diffusion control and reaction control predict that a 10-fold increase in D_e will decrease the predicted service life by a factor of 10. Therefore, reliable estimates of sulfate diffusion coefficients are needed to make reasonable service life predictions.

Methods for determining the sulfate diffusion coefficient of sulfates in cement-based materials are explored, including experimental methods and mathematical modeling. In experimental studies the depth of penetration of sulfate ions has been monitored energy dispersive x-ray analysis (EDXA) techniques. A major benefit of the radioactive tracer method is that the calcium sulfate added to the clinker will not be radioactive and thus not be detected.

Sulfate diffusion was modeled by two approaches: a finite difference model; and a "blind ant model." Both modeling approaches gave similar results. The blind ant method has the advantage that it can be applied to a specific heterogeneous microstructure, while the finite difference method is one-dimensional and must consider the microstructure to be homogeneous or at most to consist of a series of homogeneous layers. Both models show that the ingress of sulfates into concrete is highly dependent on both its diffusion coefficient and reaction constant. Further development of the models is necessary before they can be used to obtain reliable predictions of diffusion coefficients.

An approach for estimating the diffusion coefficient of sulfate ions has been developed which is based on comparing sulfate diffusion coefficients with chloride diffusion coefficients. For concretes in which portland cement is the predominant cementitious

material, a D_{eC}/D_{eS} ratio of 10 was proposed. This value can be combined with equations which predict chloride ion diffusivity as a function of w/c ratio, to estimate the sulfate diffusion coefficient.

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8. NOMENCLATURE

B - linear strain caused by one mole of sulfate reacted in 1 m^3 of concrete
C - concentration at specific depth and time
C_b - background or initial concentration
C_m - concentration at position m
C_o - concentration of sulfate ions in bulk solution
C_{oe} - concentration of reacted sulfate as ettringite,
C_s - surface concentation
c_s - sulfate concentration in bulk solution
C^+ - concentration point in time
D_e - effective diffusion coefficient
D_{eC} - effective diffusion coefficient for chloride ions
D_{eS} - effective diffusion coefficient for sulfate ions
D_i - intrinsic diffusion coefficient
D_{iA} - intrinsic diffusion coefficient of species A
E - Young's modulus
k - reaction rate constant
m - position
N - flux of sulfate ions
R_m - flag
t - time
T_{spall} - time for a layer to spall
v - Poission's ratio
w/c - water-to-cement ratio
x - depth
X_{spall} - thickness of a spalled layer

Δt - step size in time
Δx - step size in space
ϵ - porosity
σ - constriction factor
α_o - roughness factor for fracture path
τ - tortuosity factor
ψ - fracture surface energy of concrete

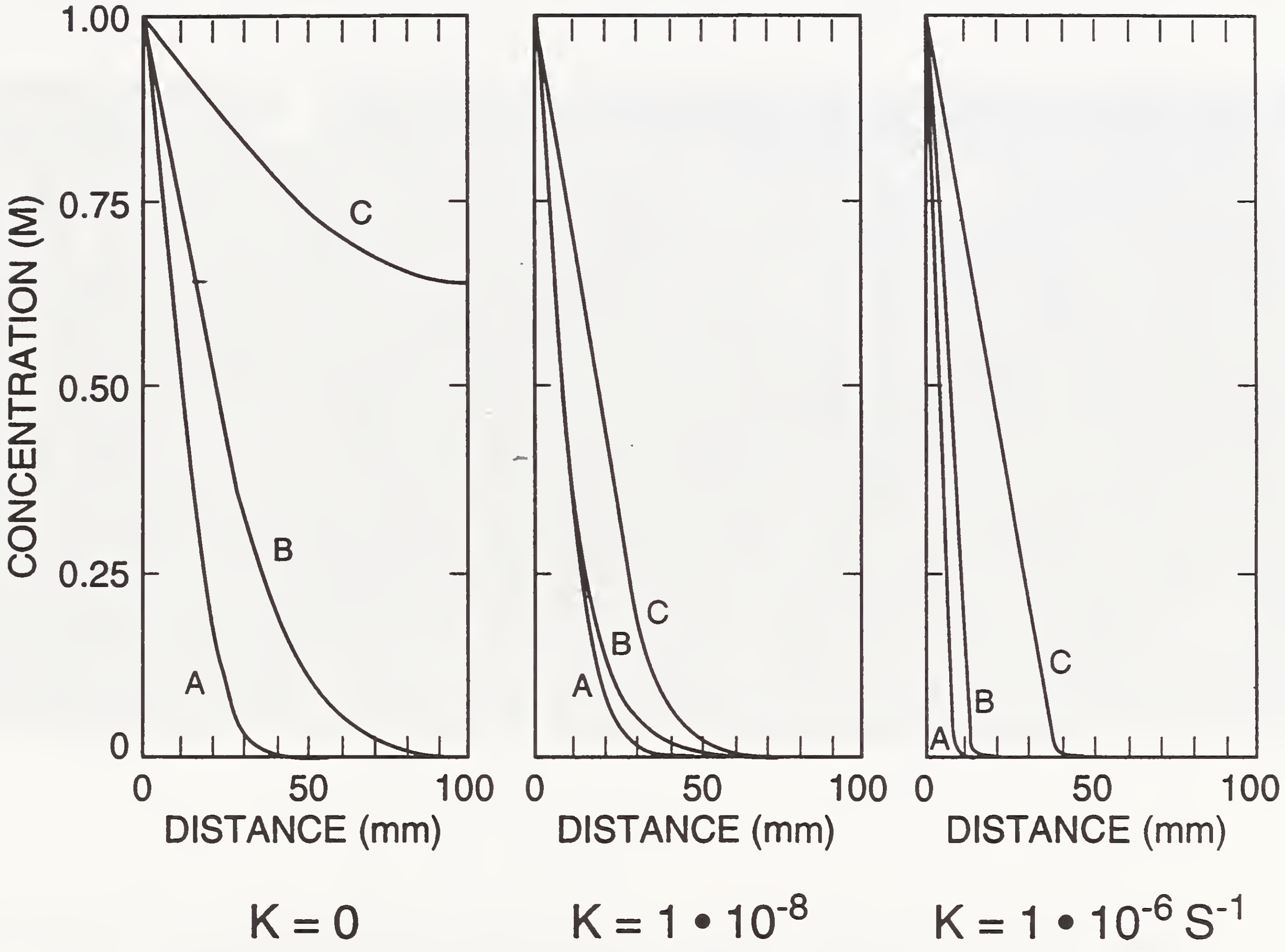

Figure 1. Concentration of diffusing sulfate in cement paste predicted by finite difference model. Exposure times to 1 N solution solution are identified by A, B, and C, having respective values of 3.2, 15.9, and 159 years. K is the reaction constant.

MICRO 2

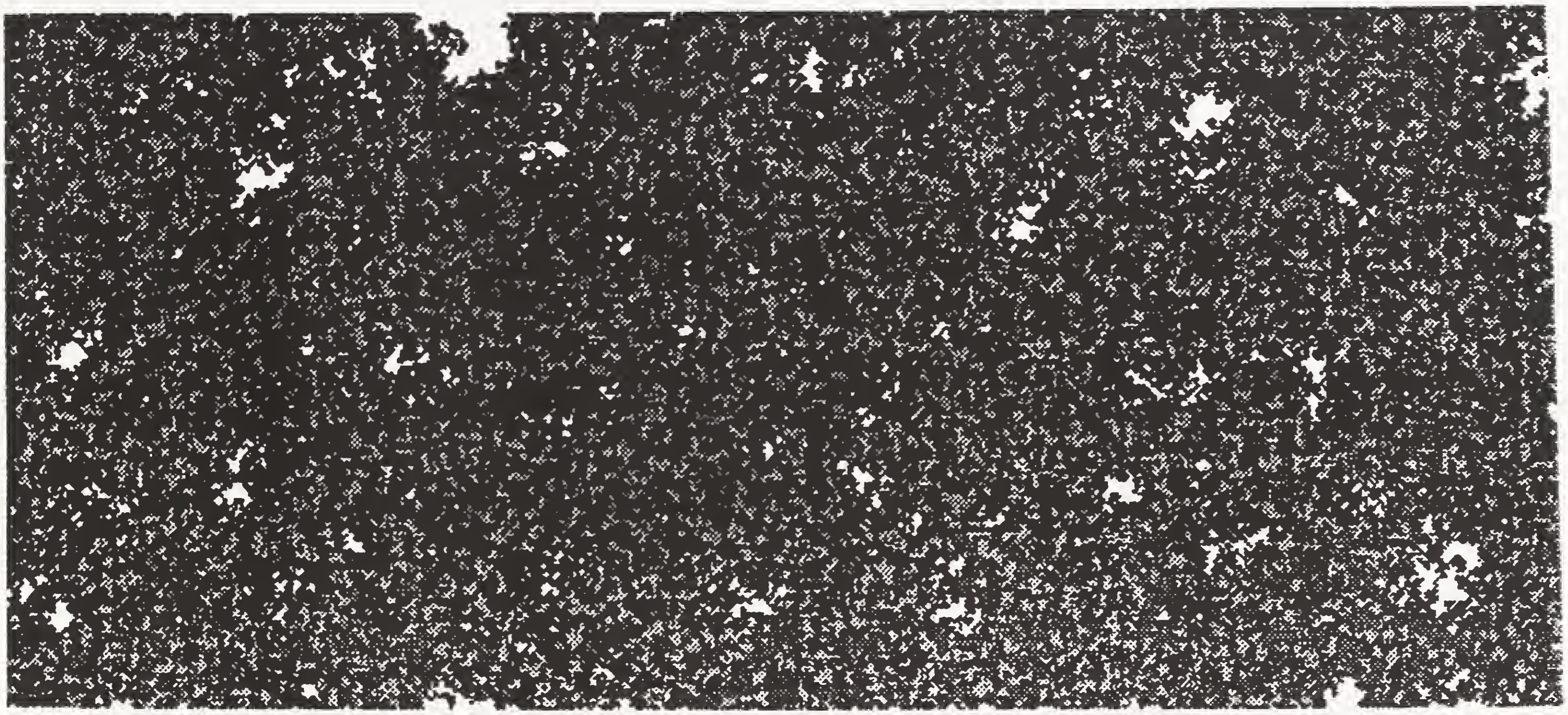

Figure 2. A 250x1000 digital image created using the NIST cement hydration microstructural model [18,19]. White indicates calcium hydroxide, light grey is unreacted cement, dark grey is C-S-H gel, and black is porosity.

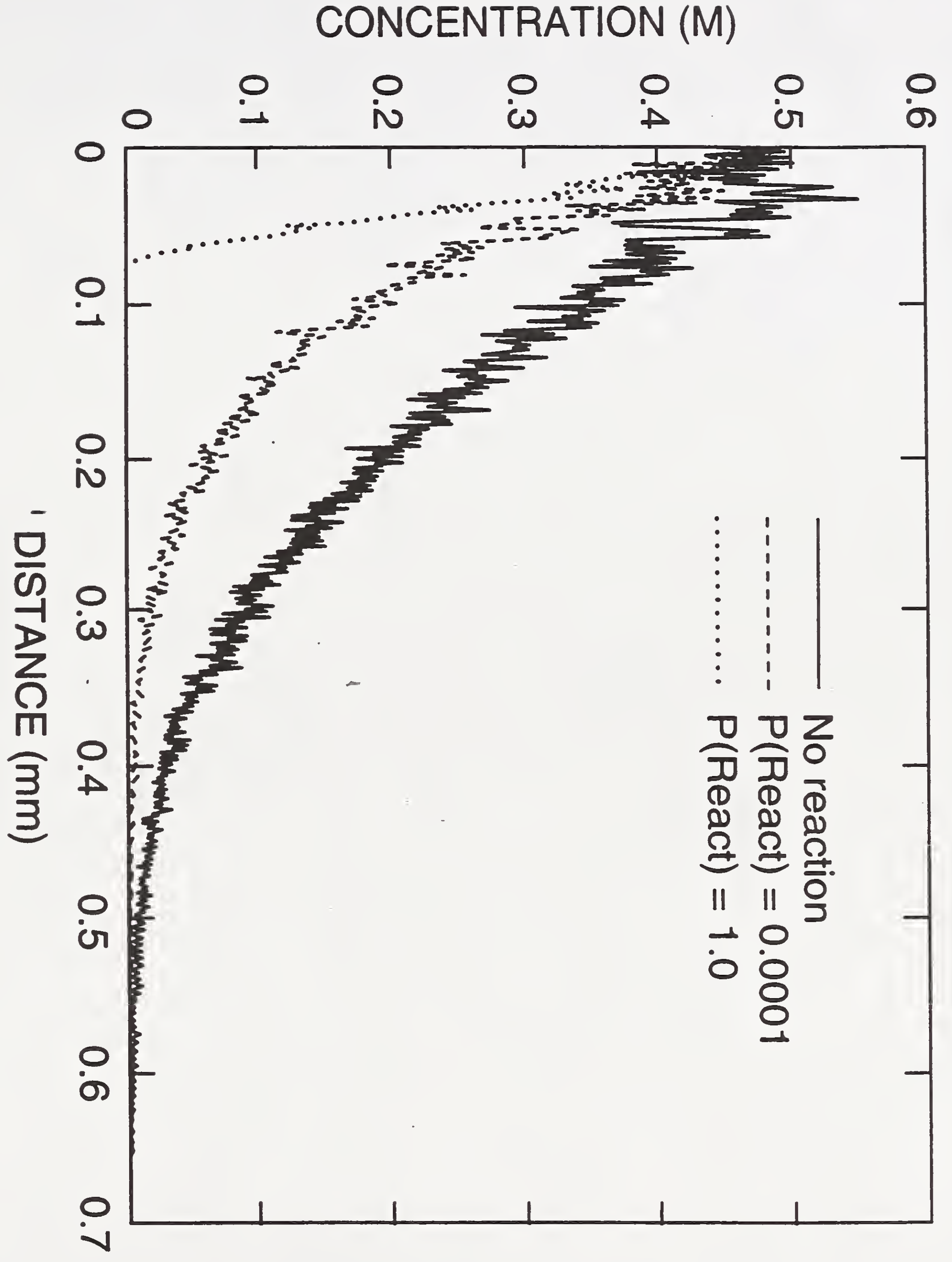

Figure 3. Concentration of diffusing sulfate in cement paste predicted by blind-ant model. P(React) is the probability of reaction.