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AN EFFECTIVE DIFFUSIVITY FOR SULFATE TRANSPORT INTO CONCRETE

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ABSTRACT

The effective non-steady state diffusivity of sulfate ingress from a mixed sulfate-chloride solution into Type 50 cement concrete was determined from concentration profiles at various times up to five years. Furthermore, the influence of CO_2 saturation on the effective diffusivity was determined. The time dependence of the effective non-steady sulfate diffusivities were,

$$\log(D_{\text{effective sulfate}}) = -6.6543 - 0.7626 \log(t)$$

and,

$$\log(D^{CO_2}_{\text{effective sulfate}}) = -6.2873 - 0.8559 \log(t)$$

where $D_{\text{effective sulfate}}$ represents the effective sulfate diffusivity, $D^{CO_2}_{\text{effective sulfate}}$ represents the effective sulfate diffusivity of the solution saturated with respect to CO_2, and t represents the time (*months*).

Introduction

The mass transport of sulfate into saturated concrete has a complex mechanism combining diffusion of the sulfate and convection of the solution due to the cracking of the concrete. Furthermore, the sulfate reacts with the hydrated cement phases. Nonetheless, with the increased acceptance of the life cycle cost analysis of concrete structures and the development of service life prediction models, it is important to determine a value of the sulfate diffusivity into concrete and its time dependence. Therefore, it was the purpose of this study to determine a zeroth order value of the effective sulfate diffusivity into concrete from mixed sulfate-chloride solutions and how this sulfate diffusivity changes with time and the presence of CO_2 in solution.

Experimental

Materials

- Binder: Type 50 Portland cement was used for the concrete. The chemical composition is given in Table 1.

TABLE 1
Chemical Compositions (%) of the Cement.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	L-O-I*	SO_3	Free Lime
19.83	4.18	3.20	61.21	4.09	0.45	0.89	1.53	3.93	1.15

*Loss on ignition.

- *Aggregate*: The fine aggregate was an unblended quartz/feldspar sand. A pelitic pemicrite limestone of 19 *mm* maximum size was the coarse aggregate. All aggregate was tested for alkali reactivity, freeze-thaw durability and defects detectable by petrographic examination.
- *Concrete*: The concrete mix design is summarized in Table 2. Beams of dimension 75 *mm* x 75 *mm* x 280 *mm* were cast and cured at 100% *rh* for 14 days. Subsequently, the beams were waxed on five sides for unidirectional sulfate ingress.

TABLE 2
Concrete Mix Design ($kg\ m^{-3}$).

Cement	Water	Fine Aggregate	Coarse Aggregate	Slump (*mm*)	Air (%)	Cure (*days*)
370.0	155.4	744.6	1117.3	131	5.9	14

The concrete beams were stored in two different solutions designated Bath 1 and Bath 2. Bath 1 had composition 22.19 $g\ l^{-1}$ Na_2SO_4 and 4.95 $g\ l^{-1}$ NaCl. Bath 2 also had the composition 22.19 $g\ l^{-1}$ Na_2SO_4 and 4.95 $g\ l^{-1}$ NaCl, but CO_2 gas was continuously bubbled through the solution which effectively saturated Bath 2 with CO_2. The solutions were maintained at 25°C temperature. After certain periods of exposure to the baths, the beams were removed. The sulfate contents were gravimetrically determined (ASTM C114) at various penetration depths using small slices dry-cut from the beam. The background sulfate content of the concrete was subtracted from the obtained results.

Results and Discussion

The sulfate penetration profile data are presented in Tables 3 and 4, for Baths 1 and 2, respectively. The profile data were fitted to a solution of Fick's second law for unsteady state diffusion in one dimension (1) given as,

$$C(x,t) = C_o\left(1-\mathrm{erf}\left(\frac{x}{\sqrt{4\cdot D_{effective}\cdot t}}\right)\right) \tag{1}$$

where, C(x,t) is the sulfate concentration for any position and time, C_o is the sulfate concentration at the surface of the concrete beam, x is the distance from the surface, t is the time, erf is the statistical error function, and $D_{effective}$ is the effective sulfate diffusion coefficient or effective sulfate diffusivity. The values for the sulfate diffusivity have been summarized in Table 5. It must be emphasized that the values reported in this study are the effective sulfate diffusivities incorporating all sulfate transport mechanisms, and the effective diffusivities do not expressly account for sulfate reaction. As such, the effective sulfate diffusivities are a zeroth order approximation of the true sulfate diffusivity.

TABLE 3
Sulfate Profile (%) for Concrete Exposed to Bath 1.

12 *Mos.*		16 *Mos.*		24 *Mos.*		60 *Mos.*	
Depth (*mm*)	% Sulfate	Depth (*mm*)	% Sulfate	Depth (*mm*)	% Sulfate	Depth (*mm*)	% Sulfate
1.5	2.724	2.15	2.050	1.8	2.656	1.9	2.622
4.1	2.090	7.5	2.011	7.2	1.723	6.0	1.63
6.0	1.634	10.95	1.915	10.85	1.424	10.0	1.624
9.45	1.602					15.9	1.497

TABLE 4
Sulfate Profile (%) for Concrete Exposed to Bath 2

16 *Mos.*		20 *Mos.*		24 *Mos.*		34 *Mos.*		46 *Mos.*	
Depth (*mm*)	% Sulfate	Depth (*mm*)	% Sulfate	Depth (*mm*)	% Sulfate	Depth (*mm*)	% Sulfate	Depth (*mm*)	% Sulfate
1.5	2.846	1.8	2.311	1.55	2.489	2.5	1.997	2.5	2.14
6.1	2.275	4.7	1.716	5.1	1.587	9.4	1.414	7.35	1.248
10.15	2.065	6.55	1.584	8.2	1.467	15.0	1.149	10.7	1.240
		10.25	1.427						

Sulfate diffusivities in concrete have not been previously reported. However, Spinks and co-workers (2) and Cabrera and Plowman (3) did report the sulfate diffusivities for cement and cement/fly ash pastes. Values for the sulfate diffusivities for the paste systems were two orders of magnitude smaller than for the concrete systems reported here (10^{-10} cm^2 s^{-1} versus 10^{-8} cm^2 s^{-1}). The observation is expected because the addition of aggregate into the cement paste introduces a significant number of additional transport paths at the aggregate-paste interface. It can also be seen from Table 5 that CO_2 increases the sulfate diffusivity probably by changing the pH of the solution to promote dissolution of the hydrated cement phases or by direct reaction of the dissolved carbonate species with the hydrated cement phases.

TABLE 5
Sulfate Diffusivities (10^8 cm^2 s^{-1})

Time (*Mos.*)	Bath 1	Bath 2
12	2.63	
16	4.73	7.50
20		2.40
24	1.31	3.10
34		2.62
46		2.19
60	1.06	

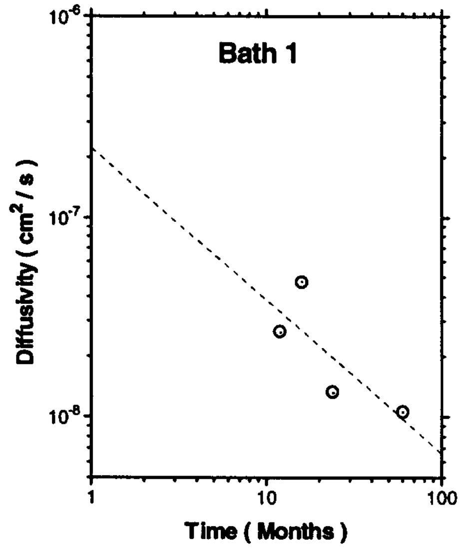

Figure 1.
Sulfate diffusivity versus time for Bath 1.

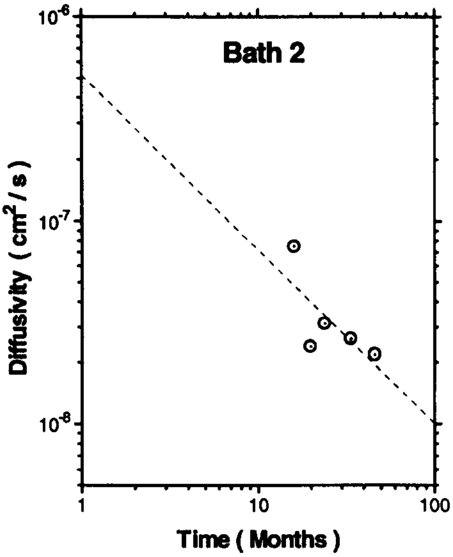

Figure 2.
Sulfate diffusivity versus time for Bath 2.

The sulfate diffusivities have been plotted against time in Figures 1 and 2 for Baths 1 and 2, respectively. The sulfate diffusivities were fit to following expressions,

[2a] $$\log (D_{\text{effective sulfate}}) = -6.6543 - 0.7626 \log (t)$$

or,

[2b] $$D_{\text{effective sulfate}} = 2.217 \times 10^{-7} \cdot t^{-0.76}$$

for Bath 1, and

[3a] $$\log (D^{CO_2}_{\text{effective sulfate}}) = -6.2873 - 0.8559 \log (t)$$

or,

[3b] $$D^{CO_2}_{\text{effective sulfate}} = 5.161 \times 10^{-7} \cdot t^{-0.86}$$

for Bath 2. In all cases, t represents the time in months. The long-term sulfate concentration profile for sulfate ingress into Type 50 cement concrete can be determined by substitution of Eq. [2] and [3] into Eq. [1] in the manner described previously (4) to give,

[4] $$C = C_o \left(1 - \text{erf} \left(\frac{x}{\sqrt{3.6945 \times 10^{-6} t^{0.24}}} \right) \right)$$

and,

[5] $$C = C_o \left(1 - \text{erf} \left(\frac{x}{\sqrt{1.4745 \times 10^{-5} t^{0.14}}} \right) \right)$$

for Bath 1 and 2, respectively.

Conclusions

- Values of the effective sulfate diffusivities in concrete are two orders of magnitude larger than those reported in the literature for the paste systems.
- The presence of CO_2 in solution increases the effective sulfate diffusivity.
- The time dependence of the effective sulfate diffusivity can be incorporated into an expression of Fick's second law for diffusion which predicts the long-term sulfate penetration profile in concrete.

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