

SULFATE DIFFUSIVITY ALTERED BY PORE CRYSTALLIZATION DUE TO CHEMICAL SULFATE ATTACK OF CEMENT-BASED MATERIALS

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Abstract

Three models are proposed for the sulfate diffusivity change due to the pore clogging by crystallization from the chemical sulfate attack of cement-based materials. The averaging model takes a linear relationship between the crystallization quantity and diffusivity change while the constriction model takes an inverse linear form and the self-consistent scheme model lies in between. These models are integrated into a diffusion-reaction model for chemical sulfate reactions in cement-based materials and solved numerically. The results show that all the three models can capture the rapid self-deceleration of sulfate ingress by fitting different relative kinetic coefficients k/D_0 and reduction parameters θ .

Keywords: cement, external sulfate attack, pore crystallization, pore refinement

1. INTRODUCTION

Sulfate attack is one of main durability concerns for concretes in saline-soil and marine environments. It leads to material expansion and spalling of cover concrete^[1] thus accelerates the penetration of other aggressive agents. The cause of expansion is widely recognized to be ettringite formation. However, recent works show that the ettringite crystals formed in pores not only cause expansion but also induce pore refinement, which decelerates the sulfate ingress^[2,3] and chloride diffusion for concrete under combined actions of sulfates and chlorides^[4]. This paper attempts to quantify the sulfate diffusivity decrease in terms of pore clogging by crystallization. To this purpose, three conceptual models are proposed and solved numerically to demonstrate their respective capacities to account for this change.

2. SULFATE DIFFUSIVITY CHANGE BY PORE CRYSTALLIZATION

2.1 Pore structure change by pore crystallization

According to Clifton et al. [5], the effective diffusivity of sulfate ions through cement-based materials is three to five orders of magnitude smaller than the diffusivity in water D' . Particularly, the pore structure reduces the diffusivity through the following mechanisms: the solid skeleton lowers the diffusion volume; the tortuosity of diffusion path increases the diffusion path length; the constricted regions offers higher diffusion resistance.

During the sulfate reactions the ettringite crystals are formed in pores, altering the pore structure and the diffusivity for subsequent ion transport, cf. Figure 1(a), (b). In terms of the above effects, the crystals will decrease globally the diffusion area and increase the constricted regions. The tortuosity can be assumed unchanged during crystallization due to the unchanged path length. The sulfate diffusivity in the liquid film, between the crystal and the solid pore wall, is judged much smaller than D' values due to the electrical double layer effect^[6] and the structured water molecules in liquid film^[8,9]. The former is due to the building-up of a repulsion potential barrier from solid surface (crystal or pore wall), and latter is attributed to the much higher viscosity of liquid film in the layered structure of water molecules in liquid film. A reduction parameter θ (<1) is adopted for the diffusivity in liquid film compared to D' .

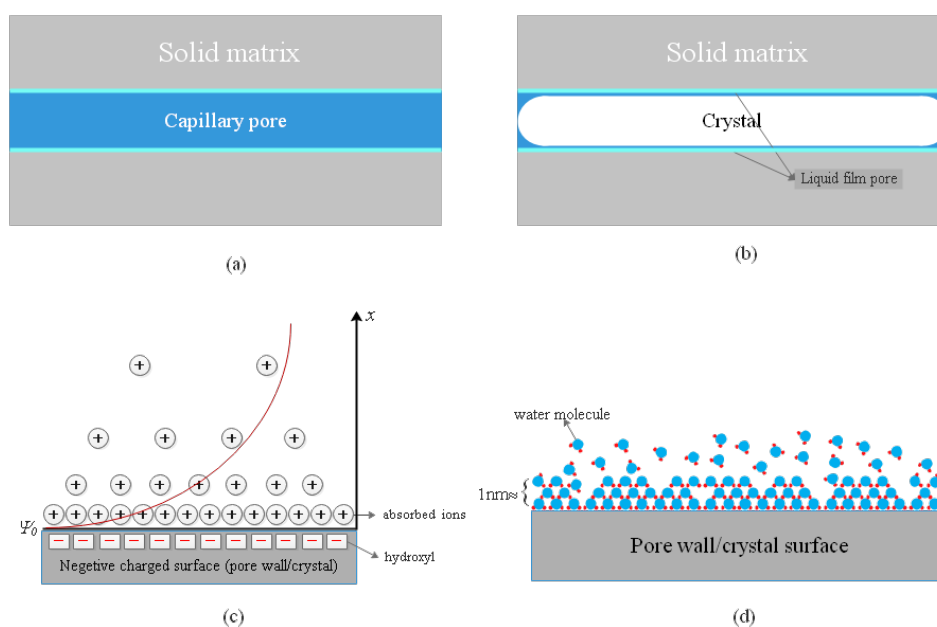


Figure 1: Diffusion path before crystallization (a), diffusion path during crystallization (b), electrical double layer on the surface (c)^[7] and layer structure of water film (d)

Accordingly, the porosity during reactions can be divided into capillary porosity ϕ_{cap} (liquid), liquid film porosity ϕ_{film} (liquid but structured) and crystal porosity ϕ_{AFt} (solid). Assume further that the deformation is negligible during the crystallization process, we can write,

$$\phi_0 = \phi_{\text{cap}} + \phi_{\text{film}} + \phi_{\text{AFt}} \quad (1)$$

where ϕ_0 is the initial porosity. In a single cylinder pore, cf. Figure 1(b), the ratio of liquid film and crystal volumes writes,

$$\alpha = \frac{\phi_{\text{film}}}{\phi_{\text{AFt}}} = \frac{4d\delta - 4\delta^2}{d^2 - 4d\delta + 4\delta^2} \text{ and } \phi_0 = \phi_{\text{cap}} + (1 + \alpha)\phi_{\text{AFt}} \quad (2)$$

where d is pore diameter and δ the thickness of film. Depending how the change of pore structure is considered for the diffusivity change, three models are proposed in the following.

2.2 Three models for diffusivity change

The first model, averaging model, considers the contribution of liquid phase, ϕ_{cap} and ϕ_{film} , on an average basis, and neglects the constriction effect. Thus, the resulted sulfate diffusivity writes,

$$D^{\text{avg}} = \phi_{\text{cap}}D^\gamma + \phi_{\text{film}}\theta D^\gamma = D^\gamma \left[\phi_0 - (1 + (1 - \theta)\alpha)\phi_{\text{AFt}} \right] \quad (3)$$

The initial diffusivity before crystallization D_0 equals to $D^\gamma\phi_0$ under the premise that all the pores are capillary pores before reaction. And the ratio between the initial sulfate diffusivity and the changed diffusivity is,

$$\frac{D^{\text{avg}}}{D_0} = 1 - \left[1 + (1 - \theta)\alpha \right] \frac{\phi_{\text{AFt}}}{\phi_0} \quad (4)$$

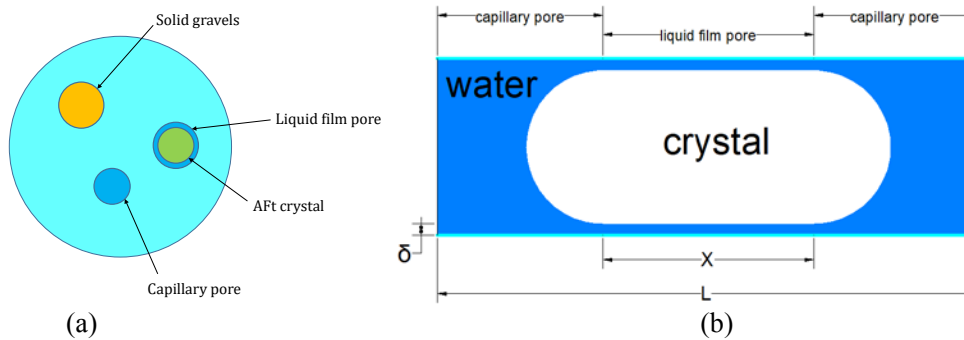


Figure 2: Material REV (a) and constriction effect by crystallization (b)

The self-consistent scheme model considers the same contribution to diffusivity but employs a homogenization scheme to describe the diffusivity change. The pores and the phases in pores are considered as the inclusions embedded in the homogeneous matrix. Taking the available results for thermal conductivity^[10], the diffusivity can be expressed as^[8],

$$D^{\text{hom}} = \overline{DA} = \overline{D_i A_i} = \sum (\phi_i D_i \overline{A_i}) \quad (5)$$

where i represents the different phases in the representative elementary volume (REV), ϕ_i , D_i and A_i represents volume fraction, diffusivity and average concentration tensor of phase i . The average concentration tensor is referred to shape geometry and spatial distribution of inclusions^[9]. Further, we assume spherical capillary pores (cap), spherical AFt crystals (AFt), and annular liquid film (film) enfolding AFt crystals and spherical solid matrix (S), cf. Figure2(a), with the diffusivity for each phase:

$$D_{\text{cap}} = D^\gamma, D_{\text{AFt}} = D_S = 0, D_{\text{film}} = \theta D^\gamma \quad (6)$$

The average concentration tensors were solved by Yang^[8] and that the homogenized diffusivity D^{hom} is,

$$D^{\text{hom}} = D^\gamma \frac{\phi_{\text{cap}} A_{\text{cap}} + \alpha \theta \phi_{\text{AFt}} A_{\text{film}}}{\phi_{\text{cap}} A_{\text{cap}} + (3/2 + \alpha) \phi_{\text{AFt}} A_{\text{film}} + (1 - \phi_0) A_S} \quad (7)$$

with,

$$A_S = \frac{3}{2}, A_{\text{AFt}} = \frac{3}{2} A_{\text{film}}, A_{\text{cap}} = \frac{3D_{\text{hom}}}{D^\gamma + 2D_{\text{hom}}}, A_{\text{film}} = \frac{3D_{\text{hom}}(\phi_{\text{AFt}} + \phi_{\text{film}})}{(3\phi_{\text{AFt}} + 2\phi_{\text{film}})D_{\text{hom}} + \phi_{\text{film}}\theta D^\gamma} \quad (8)$$

Note that the initial diffusivity without crystallization can be obtained from Eq.(7) letting $\phi_{\text{cap}} = \phi_0$ and $\phi_{\text{AFt}} = 0$. Then, the diffusivity ratio between without and with crystals is expressed as,

$$\frac{D^{\text{hom}}}{D_0} = \frac{\phi_{\text{cap}} A_{\text{cap}} + \alpha \theta \phi_{\text{AFt}} A_{\text{film}}}{\phi_{\text{cap}} A_{\text{cap}} + (3/2 + \alpha) \phi_{\text{AFt}} A_{\text{film}} + (1 - \phi_0) A_S} \cdot \frac{\phi_0 A_{\text{cap}} + (1 - \phi_0) A_S}{\phi_0 A_{\text{cap}}} \quad (9)$$

The third model, constriction model, takes into account the constriction effect of the pores filled by solid crystals (AFt), cf. Figure 2(b). Assuming the pore geometry as cylindrical, the constriction effect for diffusion can be described through connected series pores of capillary (liquid) and liquid film (semi-liquid), and the resulted diffusivity writes,

$$\frac{\phi_0}{D^{\text{csr}}} = \frac{1}{D_0} \left[\phi_{\text{cap}} + \frac{(\phi_{\text{AFt}} + \phi_{\text{film}})^2}{\theta \phi_{\text{film}}} \right] \quad (10)$$

and the diffusivity ratio between without and with crystals can be deduced as,

$$\frac{D^{\text{csr}}}{D_0} = \left[1 + \frac{(1 + \alpha)}{\alpha \theta} (1 + \alpha(1 - \theta)) \frac{\phi_{\text{AFt}}}{\phi_0} \right]^{-1} \quad (11)$$

2.3 Comparison among the three models

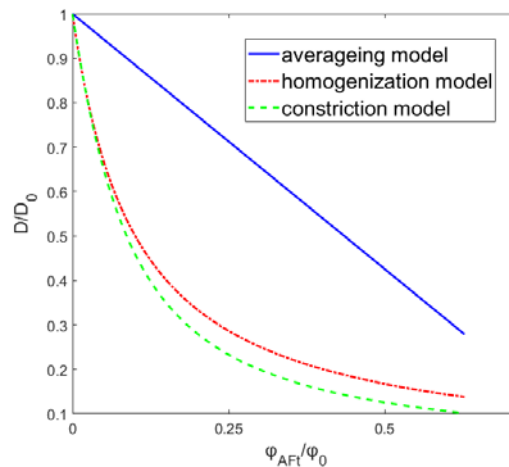


Figure 3: Comparison of three models for diffusivity change

The relations between the crystal porosity and the diffusivity ratio are illustrated in Figure 3 using Eqs.(4), (9), (11) from the three models. The averaging model shows a linear crystallization-diffusivity relation while the construction model predicts an inversely proportional relation and the self-consistent scheme model lies in between. The inversely proportional relation from constriction model indicates that a small amount of crystals can lead to a large reduction of diffusivity, which means the deceleration of sulfate ingress takes place in the very early stage of sulfate attack.

3. DIFFUSION-REACTION MODELLING FOR SULFATE ATTACK

3.1 Diffusion-reaction modelling

The diffusion-reaction model, in one dimension, is written through the mass conservation of sulfate ions in liquid phase of pores,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) - kc \quad (12)$$

where c , D are respectively the aqueous concentration of SO_4^{2-} ion (mol/L) and its diffusivity (m^2/s), k is kinetic coefficient for the crystal formation (s^{-1}). This equation assumes that the mass change of sulfate ions in pores caused by the diffusion and the crystal formation or dissolution. The crystal porosity change, $d\phi_{\text{AFt}}$, is assumed to be proportional to the consumed sulfates ions kc in crystallization,

$$d\phi_{\text{AFt}} = \nu kcdt \quad (13)$$

where ν represents the volumetric increase associated with pore crystallization of ettringite (L/mol). The diffusion coefficient of sulfate ions in Eq.(12) will consider the impact of pore crystallization, discussed in the previous section through Eqs.(4), (9) and (11).

The Eq.(12) is solved numerically through an explicit finite difference method for the fixed value boundary condition for $c(x=0, t>0) = c_0$. The algorithm is described as follows: the time-space domain $R = \{(x, t): 0 \leq x \leq L, 0 \leq t \leq T\}$ is discretized into a grid of $m-1$ by $n-1$ mesh with sizes $h=L/m$ and $\tau=T/n$. For a fixed position, $x=ih$, the sulfate concentration at the instant, $t=(j+1)\tau$, is calculated through the explicit difference scheme,

$$\frac{c_i^{j+1} - c_i^j}{\tau} = \frac{1}{h} \left[\frac{(D_{i-1}^j + D_i^j)(c_{i-1}^j - c_i^j)}{2} - \frac{(D_i^j + D_{i+1}^j)(c_i^j - c_{i+1}^j)}{2} \right] - kc_i^j \quad (14)$$

where c_i^j , D_i^j are respectively the sulfate concentration and its diffusivity at the point ($x=ih$, $t=j\tau$). Then the crystal porosity can be calculated based on the discrete scheme of Eq.(13) and substitute it into Eq(4), (9) and (11) to obtain the changed diffusivity.

3.2 Modelling results from simulations

The volume increase ratio ν is taken as $0.165^{[11]}$, and the initial porosity ϕ_0 is $0.35^{[2]}$. Then it is assumed that the average pore diameter is 20nm and thickness of liquid film is 1nm, α equals to 0.23. In a thin water channel with 1nm size, the double layer effect reduces the diffusivity to about 0.1 times of $D^{[6]}$, and the increased viscosity results in a 20% reduction in the diffusivity^[9]. Accordingly the reduction parameter θ should be less than 0.1.

By fitting two unknown parameters, relative kinetic coefficient k/D_0 and reduction parameter θ , the experimental results of relative ettringite amount in Ref. [2] can be represented through diffusion-reaction model combined with three diffusivity models in Figure 4. The fitting parameters are shown in Table 1. The values of relative kinetic coefficient k/D_0 are $0.48\text{-}1.67\text{mm}^{-2}$. The θ values from the last two models are close to 0.1. The possible reason why they exceed 0.1 is that the gel pores (liquid film pores) in C-S-H are ignored. However, to reproduce the rapid decrease of sulfate adsorption in Ref. [2] for linear crystallization-diffusivity relation from the first model, the reduction parameter should be as small as 10^{-4} .

As aforementioned, the reduction parameter is to characterize the reduction of diffusivity in liquid film pores. It depends on pore diameter and solid surface materials. And the kinetic coefficient is referred to the solution ions and the temperature.

Certainly the obtained values for these two parameters are only for model comparison purpose. To obtain the true values of these two parameters, more kinetics-based data are expected for the diffusivity change and the ettringite formation.

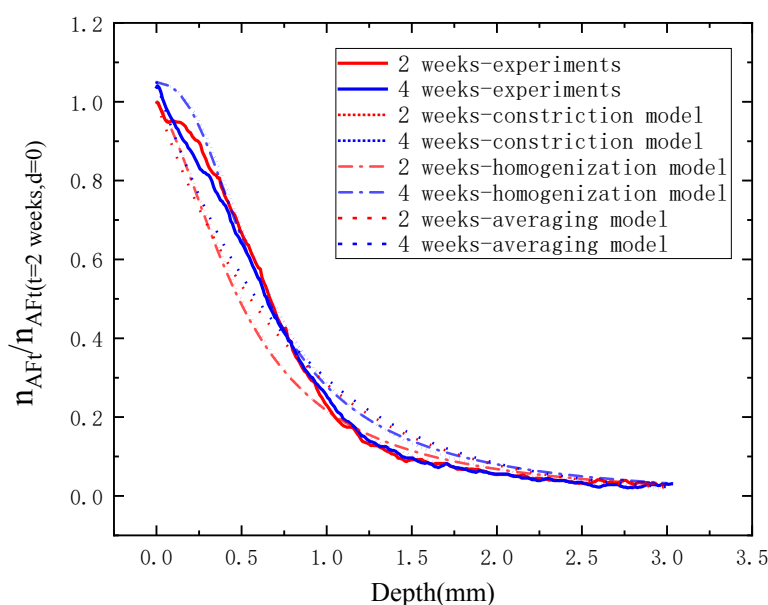


Figure 4: Relative ettringite amount in hardened cement paste in terms of diffusion depth at 2, 4 weeks of sulfate exposure. The parameters are retained as follows in the numerical simulations: $\phi_0=0.35^{[3]}$, $\alpha=0.23$, $\nu=0.165^{[11]}$, $c_0=0.3\text{ M}^{[2]}$.

Table 1: Relative kinetic coefficient and reduction parameter in three models

Diffusivity change model	k/D_0 (mm^{-2})	θ
Averaging	1.67	0.0001
Homogenization	0.48	0.15
Constriction	0.95	0.35

4. CONCLUSIONS

- The change of sulfate diffusivity of cement-based materials by pore crystallization during chemical sulfate attack is addressed through three models: the averaging model, self-consistent scheme model and constriction model. All these models can describe the diffusivity decrease by pore crystallization and the constriction model gives most rapid decrease with the AFt formation.
- From a conceptual diffusion-reaction model for chemical sulfate attack, the rapid decrease of sulfate adsorption observed in experiments can be explained by the reduction of diffusivity in three proposed models. And a further study should be conducted to measure the kinetic coefficient and reduction parameter.

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