A composite-material model for the chloride diffusivity of unracked and microcracked concrete

Fagerlund, Göran

1993

Citation for published version (APA):
A composite-material model for the chloride diffusivity of uncracked and microcracked concrete

Göran Fagerlund

Presented at The Nordic Seminar on Chloride Penetration in Concrete held at the Division of Building Materials, Chalmers University of Technology, Gothenburg January 13-14, 1993

Rapport TVBM-7037
Lund, January 1993
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>1</td>
</tr>
<tr>
<td>1. The basic composite-material model</td>
<td>1</td>
</tr>
<tr>
<td>2. Assumptions</td>
<td>2</td>
</tr>
<tr>
<td>3. The diffusivity of the uncracked concrete</td>
<td>4</td>
</tr>
<tr>
<td>3.1 The theoretical model - constant diffusivity in gel pores and capillary pores</td>
<td>4</td>
</tr>
<tr>
<td>3.2 The theoretical model - variable diffusivity in gel pores and capillary pores</td>
<td>6</td>
</tr>
<tr>
<td>3.3 Application of the model in 3.1</td>
<td>7</td>
</tr>
<tr>
<td>4. The diffusivity of microcracked concrete</td>
<td>9</td>
</tr>
<tr>
<td>4.1 Discontinuous crack systems</td>
<td>9</td>
</tr>
<tr>
<td>4.2 Continuous crack systems</td>
<td>10</td>
</tr>
<tr>
<td>4.3 Application of the model</td>
<td>10</td>
</tr>
<tr>
<td>Literature</td>
<td>12</td>
</tr>
<tr>
<td>Tables</td>
<td>13</td>
</tr>
<tr>
<td>Figures</td>
<td>15</td>
</tr>
</tbody>
</table>
A simple composite-material model is utilized for calculating the chloride diffusivity of concrete. In the model a distinction is made between two basic cases; (i) the matrix is much more permeable than the particle phase, (ii) the particle phase is much more permeable than the matrix. This means that two types of equations are used for calculating the global diffusivity. The diffusivity of chlorides in coarse pores (capillary pores) is supposed to be the same as the diffusivity of chlorides in bulk solution. The diffusivity in very narrow pores (gel pores) is supposed to be influenced by surface effects and chemical reaction with the solid material, Thus, it is lower than the diffusivity in bulk solution. The diffusivities of the two pore systems are, as first approximation, supposed to be independent of the w/c-ratio and the degree of hydration. A method to consider an eventual effect of the w/c-ratio is suggested.

The uncracked concrete is divided in four sub-systems each one being analyzed separately. In a microcracked concrete a fifth sub-system is used, the cracks being either particle phase (in the case of discontinuous cracks) or matrix phase (in the case of continuous cracks or cracks open to the concrete surface).

An important feature of the model is that the diffusivity of concretes with w/c-ratio below 0.63 is drastically reduced at a certain "critical" degree of hydration. The physical reason for this is that the volume fraction of the cement gel phase, after a certain hydration, is large enough to block all coarse pores making the capillary pore system an isolated particle phase.

The analysis of the effect of cracks indicate that isolated microcracks will have a marginal effect on the diffusivity of the concrete unless the frequency and width of such cracks are exceptionally large. Continuous cracks, on the other hand, will have a large effect on the diffusivity, especially for dense concretes with low w/c-ratios.

1. The basic composite-material model

The material is on all levels supposed to be composed of particles enclosed in a continuous phase, the matrix. The particles and the matrix are more or less permeable to chlorides. The simplest composite-material models imaginable are the parallel and the series model. They result in the following general equation for the diffusivity, $\delta$, of the composite material:

$$\delta^n = v_p \delta_p^n + v_m \delta_m^n$$  (1)
where \( v_p \) and \( v_m \) are the particle and the matrix volume fractions respectively and \( \delta_p \) and \( \delta_m \) are the diffusivities of the two phases. The exponent \( n \) is -1 for the series model and +1 for the parallel model. When \( \delta_m \gg \delta_p \) the parallel model is most reasonable while the series model is most reasonable for \( \delta_p \gg \delta_m \). For a real material neither the parallel model nor the series model can be applied. As pointed out by Hillerborg /1/ eq (1) can nevertheless be applied to a real material provided the exponent \( n \) is selected in a careful way within the range \( -1 < n < +1 \) and provided \( n \neq 0 \). Hillerborg shows that \( n > 0 \) for materials in which the matrix is more permeable than the particle phase while \( n < 0 \) for materials in which the opposite is the case. Hillerborg gives recommendations for how to select a proper value of the exponent \( n \) for different values of the ratio \( \delta_p/\delta_m \). The expression so obtained give similar results as those obtained by more complicated composite-material expressions such as the Hashin formula.

Hillerborg /1/ shows that the following values can be used when the difference in diffusivities between the two phases is large: \( n = +0.5 \) for \( \delta_m \gg \delta_p \) and \( n = -0.5 \) for \( \delta_p \gg \delta_m \). Thus, eq (1) with \( n = +0.5 \) or \( n = -0.5 \) is the general equation used further on.

2. Assumptions

The calculations below are based on the following assumptions:

* The diffusivity of the cement gel is constant for each w/c-ratio and each degree of hydration. In other words, exactly the same type of cement gel is supposed to be produced for all concrete compositions at all concrete ages. This is probably an oversimplification. There are some observations indicating that cement gel produced at later stages of hydration or in very dense cement pastes has a somewhat different chemical composition than ordinary cement gel and therefore probably a different pore structure, a different chloride binding capacity and a different diffusivity. Therefore, the effective diffusivity of this more dense gel is probably lower than for "normal" cement gel.

* All adsorption or chemical reaction of chlorides is supposed to take place in the cement gel. Therefore, the effective diffusivity is much lower in the cement gel pores than in capillary pores. The difference in effective diffusivity between gel pores and capillaries is supposed to be due solely to those chloride binding effects.

The relative diffusivity between gel pores \( \delta_{gp} \) and capillary pores \( \delta_{cp} \) is defined:

\[
\delta_{gp}/\delta_{cp} = \beta \quad \beta < 1
\]  

(2)
where, as said above, the coefficient $\beta$ is, as a first approximation, supposed to be independent of the w/c-ratio and degree of hydration.

* The diffusivity in cracks, $\delta_{cr}$, or in capillary pores, $\delta_{cp}$, is, as a first approximation, supposed to be the same as the diffusivity $\delta_0$ of chlorides in free chloride solutions. A typical value for NaCl-diffusion in water is /2/:

$$\delta_{cr} = \delta_{cp} = \delta_0 = 1.5 \times 10^{-9} \text{ m}^2/\text{s}$$  (3)

* The diffusivity of solid gel or unhydrated cement particles is supposed to be 0.

* Interfacial zones between aggregate particles (especially the coarse particles) and cement paste are neglected. Hence, all space between aggregate particles is supposed to be composed of undisturbed, bulk cement paste. This is not a correct assumption since a considerable fraction of the paste is composed of an interface zone with somewhat different properties compared to the bulk paste; larger porosity, other chemical composition etc. An approximative calculation based on measurements of the thickness of the interface zone /3,4/ and the specific area of the aggregate shows that the volume of this zone can be as high as 20% of the total cement paste volume, or even more. The effect of the interface zone can be easily considered in a composite-material model by dividing the cement paste in two phases; the bulk phase and the interface phase having somewhat different diffusivities. Such a model has been used by Hedenblad /5/ to explain the difference in moisture transport properties between cement paste or mortar and concrete. Such a correction is, however, not made in the actual report.

* The volumes of all cement paste components are calculated by formulas presented in /6/ and are mainly based on Powers' work /7/.

* The cement is supposed to be of type ordinary portland. The formulas are such, however, that any cement can be used provided relevant figures are inserted for the diffusivity of the gel pore system and for the volumae fractions of different components of the cement paste.

* Air pores are supposed to stay airfilled. Therefore, they do not take part in the chloride diffusion process.
3. The diffusivity of the uncracked concrete

3.1 The theoretical model - constant diffusivity in gel pores and capillary pores

The concrete is divided in 4 sub-systems:

System 1: Cement gel particles (p) in a gel pore matrix (m). The gel porosity is 28%.

\[ \nu_p = 0.72 \quad \delta_p = 0 \]
\[ \nu_m = 0.28 \quad \delta_m = \delta_{gp} = \beta \cdot \delta_{cp} \quad \text{(Constant for all w/c-ratios and degrees of hydratation)} \]
\[ \delta_m >> \delta_p \quad \text{which gives} \quad n = +0.5 \]

Eq (1) gives:
\[ \delta_1^{0.5} = 0.28 \cdot (\beta \cdot \delta_{cp})^{0.5} \]
\[ \delta_1 = 0.078 \cdot \beta \cdot \delta_{cp} \quad \text{(4)} \]

System 2: Unhydrated cement grains (p) in a cement gel matrix (m).

\[ V_{total} = (0.32 + 0.39 \cdot \alpha) \cdot c \]
\[ \nu_p = 0.32 \cdot (1 - \alpha)/(0.32 + 0.39 \cdot \alpha) \quad \delta_p = 0 \]
\[ \nu_m = 0.71 \cdot \alpha/(0.32 + 0.39 \cdot \alpha) \quad \delta_m = \delta_1 \quad \text{according to eq (4)} \]

Where \( \alpha \) is the degree of hydration and \( c \) is the cement content of the cement paste in kg/litre.
\[ \delta_m >> \delta_p \quad \text{which gives} \quad n = +0.5 \]

Eq (1) gives
\[ \delta_2^{0.5} = [0.71 \cdot \alpha/(0.32 + 0.39 \cdot \alpha)] \cdot \delta_1^{0.5} \]
\[ \delta_2 = [0.71 \cdot \alpha/(0.32 + 0.39 \cdot \alpha)]^{2} \cdot \delta_1 \quad \text{(5)} \]

Insertion of eq(4) in (5) gives:
\[ \delta_2 = [0.71 \cdot \alpha/(0.32 + 0.39 \cdot \alpha)]^{2} \cdot 0.078 \cdot \beta \cdot \delta_{cp} \quad \text{(6)} \]
\[ \delta_2 = k \cdot \alpha \cdot \beta \cdot \delta_{cp} \quad \text{(6') \]

-4-
The coefficient $k_\alpha$ is thus a function of the degree of hydration:

\[
\begin{align*}
\alpha = 0 & \quad k_\alpha = 0 \\
\alpha = 0.25 & \quad k_\alpha = 1.41 \times 10^{-2} \\
\alpha = 0.50 & \quad k_\alpha = 3.71 \times 10^{-2} \\
\alpha = 0.75 & \quad k_\alpha = 5.90 \times 10^{-2} \\
\alpha = 1 & \quad k_\alpha = 7.80 \times 10^{-2}
\end{align*}
\]

The diffusivity $\delta_2$ calculated by eq (6') is independent of the w/c-ratio and it is the same for each constant degree of hydration. The effect of the hydration state is only considered in the volume fractions to be used in the composite-material equation (6). It might be, however, that the diffusivity of the gel pores, $\delta_{gp}$, is a function of w/c, especially for w/c-values below 0.39 which is the maximum value for complete hydration of pure portland cement pastes. It might also be that it is a function of the hydration state since the chloride binding capacity of the gel might change with time. The effects of those two factors can be considered by letting the diffusivity ratio $\beta$ be a function of the w/c-ratio and the actual degree of hydration and not be a constant as suggested above. A method to consider the effect of the w/c-ratio is discussed in 3.2.

**System 3:** All cement paste exclusive of air-filled air pores. Thus, system 3 consists of the capillary pore system and the system 2 above. The capillary pore system is matrix phase when the volume fraction of system 2 is too small to completely block all continuous capillaries. The capillary pore system is particle phase when the volume of system 2 is large enough to isolate all capillaries. The transition from the two phase systems is supposed to occur when system 2 just reaches a close-packed structure. As shown in /6/ this occurs at a certain critical degree of hydration, $\alpha_0$, which is proportional to the w/c-ratio:

\[
\alpha_0 = 1.90 \cdot w/c - 0.21
\]  

\[
V_{\text{total}} = (w/c + 0.32) \cdot c
\]

Where w is the water content of the fresh cement paste in kg/litre.

**Below $\alpha_0$:**

\[
\begin{align*}
\delta_p &= \delta_2 \text{ (eq (6'))} \\
\delta_m &= \delta_{cp} \\
\delta_m &>> \delta_p \quad \text{which gives} \quad = +0.5
\end{align*}
\]
Above $\alpha_0$: $v_p = v_{\text{capillary pores}} = \text{see above}$
$\delta_p = \delta_{cp}$
$v_m = v_{\text{system 2}} = \text{see above}$
$\delta_m = \delta_2$
$\delta_p >> \delta_m$ which gives $n = -0.5$

A general composite-material formula based on eq (1) is therefore:

$$\delta_3 = \left[ (0.32 + 0.39\cdot\alpha)/(w/c + 0.32) \cdot (k_{\alpha, \beta})^n + (w/c - 0.39\cdot\alpha)/(w/c + 0.32) \right]^{1/n} \cdot \delta_{cp} \quad (8)$$

Where $n = +0.5$ for $\alpha < \alpha_0$ and $n = -0.5$ for $\alpha > \alpha_0$.

This means that the cement paste diffusivity $\delta_3$ makes a jump at $\alpha = \alpha_0$. Cement pastes with a w/c-ratio above 0.63 will, however, never undergo such a change in diffusivity. The gel volume will not be large enough to block the capillaries even at complete hydration; see eq (7).

**System 4**: Aggregate is particle phase (p) in a cement paste matrix (m).

$v_p = v_{\text{aggregate}}$  \quad $\delta_p = 0$
$v_m = v_{\text{cement paste}}$  \quad $\delta_m = \delta_3$ according to eq (8)
$\delta_m >> \delta_p$ which gives $n = +0.5$.

Eq(1) gives:

$$\delta_{\text{concrete}} = v_{\text{cement paste}}^2 \cdot \delta_3 \quad (9)$$

### 3.2 The theoretical model - variable diffusivities in gel pores and capillary pores

Only the effect of the w/c-ratio is analysed. The eventual effect of the degree of hydration on the effective diffusivity in the cement gel is neglected.

The diffusivity in the gel pores is supposed to be a function of the w/c-ratio. The following relation is used:

$$\delta_{gp}/\delta_0 = \beta_{w/c} \quad (10)$$

$$\beta_{w/c} = f(w/c) \quad (11)$$
Where $\delta_0$ is the diffusivity of chloride ions in a bulk solution and $\beta_{w/c}$ is a coefficient which is a function of the w/c-ratio; the lower the w/c-ratio the lower the value of $\beta_{w/c}$.

The diffusivity in capillary pores is also supposed to be a function of the w/c-ratio. The following relation is suggested.

$$\frac{\delta_{cp}}{\delta_0} = \gamma_{w/c}$$  \hspace{1cm} (12)

$$\gamma_{w/c} = g(w/c)$$  \hspace{1cm} (13)

The coefficient $\gamma_{w/c}$ is a function of the w/c-ratio. No quantitative expressions for $\beta_{w/c}$ and $\gamma_{w/c}$ are suggested here.

The final expression for the diffusivity of the cement paste is:

$$\delta_3 = [(0,32 + 0,39\cdot\alpha)/(w/c + 0,32)^\gamma_{w/c} + (w/c + 0,39\cdot\alpha)/(w/c + 0,32)^{n+1}/n_\delta_0]$$  \hspace{1cm} (14)

Where the coefficient $k_\alpha$ is the same as in eq (8).

3.3 Application of the model in 3.1

Some practical applications of the equations derived in section 3.1 above will be shown. Only the diffusivity of the cement paste phase will be calculated. The concrete diffusivity is approximately directly proportional to the cement paste diffusivity; see eq (9).

**Application 1:** The diffusivity in gel pores is 30% of the diffusivity in capillary pores. Hence, $\beta=0,3$.

The results of the calculations are shown in Table 1.

The values are also plotted in Fig 1. The jump in the diffusivity curve at $\alpha_0$ is evident. In reality, the transition from a high to a low diffusivity occurs more gradually than calculated here. Such a gradual transition can be considered mathematically by letting the exponent $n$ in eq (8) change gradually from +0,5 to -0,5 over a certain limited interval of degree of hydration. It can also be considered physically by letting the diffusivity of the capillary pore system be a function of the capillary porosity.
Such transitions from a high to a low permeability over a certain rather narrow porosity range have been observed previously for cement paste exposed to flow of liquid water under external pressure.

For some cement pastes, Table 1 indicates that there is a certain increase in the diffusivity for increasing degree of hydration when this is higher than $\alpha_0$. This is of course not possible. The reason is that the exponent $n$ in eq(1) has been supposed to be constant; either +0.5 or -0.5. In reality, the exponent is a function of the real ratio between the diffusivities of the two phases. Hence, the real value changes a bit with the degree of hydration. When this is considered, a monotonously falling diffusivity with increasing degree of hydration is obtained.

The diffusivity as a function of the w/c-ratio at the constant degree of hydration 0.50 is relatively well described by the equation:

$$\delta_3 = 0.60 \cdot (w/c)^{1.7} \cdot \delta_{cp} \; \text{ for } \alpha = 0.50 \; \text{and } \alpha < \alpha_0 \; (w/c > 0.37) \; \text{(15)}$$

Similar expressions, but with somewhat larger values of the exponent have previously been found to be valid for diffusion of water and gases through concrete.

Inserting the value $\delta_{cp} = 1.5 \cdot 10^{-9}$ m$^2$/s -eq(3)- gives the following diffusivities for cement pastes with 75% degree of hydration:

- w/c = 0.30: $\delta_3 = 2.7 \cdot 10^{-11}$ m$^2$/s
- w/c = 0.40: $\delta_3 = 3.5 \cdot 10^{-11}$
- w/c = 0.50: $\delta_3 = 4.35 \cdot 10^{-11}$
- w/c = 0.60: $\delta_3 = 26.9 \cdot 10^{-11}$

The values are about five to ten times as large as measured values. Possible explanations are:

* The ratio of diffusivity in gel pores and capillary pores is smaller than the suggested value 0.3.
* The real diffusivity of chlorides in capillary pores is about five to ten times as small as the diffusivity in bulk solutions.

Both explanations are reasonable. The first one will be examined below in Application 2.
**Application 2:** The diffusivity in gel pores is only 1% of the diffusivity in capillary pores. Hence, $\beta = 0.01$.

The results of the calculations are shown in Table 2.

The values are also plotted in Fig 3. The following diffusivities are obtained for 75% hydration when the capillary pores are supposed to have the diffusivity $\delta_{cp} = 1.5 \times 10^{-9}$ m$^2$/s.

\[
\begin{align*}
\text{w/c} = 0.30: & \quad \delta_3 = 0.91 \times 10^{-12} \text{ m}^2/\text{s} \\
\text{w/c} = 0.40: & \quad \delta_3 = 1.22 \times 10^{-12} \\
\text{w/c} = 0.50: & \quad \delta_3 = 1.56 \times 10^{-12} \\
\text{w/c} = 0.60: & \quad \delta_3 = 1.84 \times 10^{-12}
\end{align*}
\]

The diffusivities are now only 3 to 5% of the values in the previous calculation and are more close to the observed values. The effect of the w/c-ratio is however rather small when the hydration is below the critical hydration causing the capillary pore system to close. For 50% hydration and below the critical hydration, and for 75% hydration and above the critical hydration the theoretical expressions in eq (16) and (17) below fit the calculated data with good precision:

\[
\begin{align*}
\delta_3 &= 0.56 (w/c)^2 \delta_{cp} \quad \text{for } \alpha = 0.50 \text{ and } \alpha < \alpha_0 \text{ (w/c > 0.37)} \quad (16) \\
\delta_3 &= 2 \cdot w/c \delta_{cp} \quad \text{for } \alpha = 0.75 \text{ and } \alpha > \alpha_0 \text{ (w/c < 0.51)} \quad (17)
\end{align*}
\]

A larger effect of the w/c-ratio will be obtained if the coefficient $\beta$ expressing the relation between the diffusivity in gel pores and in capillary pores is supposed to be depending of the w/c ratio and/or if the diffusivity of the capillary pores is assumed to be a function of the w/c-ratio. A method to consider those effects of the w/c-ratio is presented in eq (14) above.

4. **The diffusivity of microcracked concrete**

4.1 **Discontinuous crack systems**

The cracks are supposed to be thin and with limited extension. Hence, they are supposed to be particle phase (p) in the cement paste matrix (m).
\( v_p = v_{\text{cracks}} = \varepsilon \cdot v_{\text{total}} \quad \delta_p = \delta_0 \) the chloride diffusivity in bulk solution \( = 1.5 \cdot 10^{-9} \)

\( v_m = v_{\text{paste}} = (1-\varepsilon) \cdot v_{\text{total}} \quad \delta_m = \delta_3 \) according to eq (8) or (14)

\( \delta_p >> \delta_m \) which means that the exponent \( n = -0.5 \).

\[ \delta_3' = [\varepsilon \cdot \delta_0^{-0.5} + (1 - \varepsilon) \cdot \delta_3^{-0.5}]^{-2} \] (18)

Where \( \delta_3' \) is the diffusivity of the cracked concrete. The equation can be simplified by utilizing the following definition:

\[ \delta_0/\delta_3 = \theta \] (19)

\[ \delta_3'/\delta_3 = [\varepsilon \cdot \theta^{-0.5} + (1 - \varepsilon)]^{-2} \] (20)

4.2 Continuous crack systems

The cracks are supposed to be long and interconnected, or they are open to the free concrete surface. Then, the cracked paste consists of two continuous phases which means that, in the most extreme case, the parallell material model can be applied. Hence, \( n = +1 \). However, in the following, the material is supposed to be particulate with the cracks being the continuous phase.

\( \delta_m >> \delta_p \) which means that \( n = +0.5 \)

The following relation is valid:

\[ \delta_3'/\delta_3 = [\varepsilon \cdot \theta^{0.5} + (1-\varepsilon)]^2 \] (21)

4.3 Application of the model

Calculated diffusivities for some values of the parameters \( \varepsilon \) and \( \theta \) are shown in table 3. and are plotted in Fig 3.
Example 1; Densely spaced microcracks in dense cement paste:
The crack width is assumed to be only 1 \( \mu \)m. The average spacing between the cracks is assumed to be of the same order of size as the spacing between individual cement grains. This is about 10 \( \mu \)m. The w/c-ratio is supposed to be 0.4 and the degree of hydration is 75%. Then, the following parameters are valid:

\[ \varepsilon = \frac{1}{10} = 0.1 \quad \text{(Linear cracks)} \]
\[ \theta = \frac{1}{8} \cdot 1.10^{-4} = 1.23 \cdot 10^{-3} \quad \text{(Table 2)} \]

Discontinuous cracks: \( \delta_3/\delta_3 = 1.23 \)
Continuous cracks: \( \delta_3/\delta_3 = 19.5 \)

Example 2; Widely spaced microcracks in dense cement paste:
The same concrete and the same crack width as in example 1, i.e. 1 \( \mu \)m but the spacing is of the same order of size as the spacing between individual sand grains which is about 100 \( \mu \)m. Thus:

\[ \varepsilon = \frac{1}{100} = 0.01 \]
\[ \theta = 1.23 \cdot 10^{-3} \quad \text{(the same as in example 1)} \]

Discontinuous cracks: \( \delta_3/\delta_3 = 1.02 \)
Continuous cracks: \( \delta_3/\delta_3 = 1.80 \)

Example 3; Densely spaced microcracks in "permeable" cement paste:
The same conditions as in example 1 but the cement paste has a w/c-ratio of 0.60 and the degree of hydration is 75%. For this paste \( \delta_3/\delta_0 = 0.123 \). Then the parameters \( \varepsilon \) and \( \theta \) have the values:

\[ \varepsilon = 0.1 \quad \text{(Example 1)} \]
\[ \theta = \frac{1}{0.123} = 8.1 \quad \text{(Table 2)} \]

Discontinuous cracks: \( \delta_3/\delta_3 = 1.14 \)
Continuous cracks: \( \delta_3/\delta_3 = 1.40 \)
Those examples show that a small amount of discontinuous microcracks has a marginal effect on the diffusivity unless they are very closely spaced. Even then, the diffusivity does not increase by more than 25 to 50%. Continuous cracks, on the other hand, will have a very large effect on the diffusivity even when the amount of cracking is fairly low. The relative effect is higher the lower the w/c-ratio. Therefore, continuous "open" cracks cannot be neglected when estimating the diffusivity of concrete.

Literature


/2/ Handbook of Chemistry and Physics.


Table 1: The diffusivity of the cement paste, $\delta_3/\delta_{cp}$, when $\beta = 0.3$.

<table>
<thead>
<tr>
<th>w/c</th>
<th>$\alpha$</th>
<th>$\delta_3/\delta_{cp}$</th>
<th>$\alpha_0$</th>
<th>$\delta_3/\delta_{cp}$ in the vicinity of $\alpha_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\alpha_0 - \Delta\alpha$</td>
</tr>
<tr>
<td>0.30</td>
<td>0</td>
<td>0.234</td>
<td></td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.137</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.015</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.018</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>0</td>
<td>0.310</td>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.210</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.130</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.023</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>0</td>
<td>0.372</td>
<td></td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.275</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.192</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.029</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.60</td>
<td>0</td>
<td>0.425</td>
<td></td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.331</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.249</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.179</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.036</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2: The diffusivity of the cement paste, $\delta_3/\delta_{cp}$, when $\beta = 0.01$

<table>
<thead>
<tr>
<th>w/c</th>
<th>$\alpha$</th>
<th>$\delta_3/\delta_{cp}$</th>
<th>$\alpha_0$ {eq (6)}</th>
<th>$\delta_3/\delta_{cp}$ in the vicinity of $\alpha_0$</th>
<th>$\alpha_0 - \Delta\alpha$</th>
<th>$\alpha_0 + \Delta\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>0</td>
<td>0.234</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.112</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.000043</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.000060</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>0</td>
<td>0.310</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.182</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.089</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.000081</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.000080</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>0</td>
<td>0.372</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.247</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.147</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.0010</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.0010</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.60</td>
<td>0</td>
<td>0.425</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.304</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.203</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.123</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.0013</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3: The relative diffusivity $\delta_3/\delta_3$ of cracked cement paste

<table>
<thead>
<tr>
<th>$\varepsilon$</th>
<th>Type of cracks</th>
<th>$\theta = 10$</th>
<th>$\theta = 10^2$</th>
<th>$\theta = 10^3$</th>
<th>$\theta = 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>discont.</td>
<td>1.15</td>
<td>1.21</td>
<td>1.23</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>cont.</td>
<td>1.48</td>
<td>3.61</td>
<td>16.5</td>
<td>119</td>
</tr>
<tr>
<td>0.01</td>
<td>discont.</td>
<td>1.01</td>
<td>1.02</td>
<td>1.02</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>cont.</td>
<td>1.04</td>
<td>1.19</td>
<td>1.71</td>
<td>3.96</td>
</tr>
<tr>
<td>0.001</td>
<td>discont.</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>cont.</td>
<td>1.00</td>
<td>1.02</td>
<td>1.06</td>
<td>1.21</td>
</tr>
</tbody>
</table>
Fig 1: The relative diffusivity, $\delta_2/\delta_{cp}$, of the cement paste when the ratio $\beta$ between the diffusivities in gel pores and capillary pores is 0.3.
Fig 2: The relative diffusivity, $\delta_3/\delta_{cp}$, of the cement paste when the ratio $\beta$ between the diffusivities in gel pores and capillary pores is 0.01.
Fig 3: The diffusivity of microcracked concrete relative to the diffusivity of uncracked concrete. Continuous crack system.