

Origin of chloride diffusivity of cement pastes – a scale transition analysis

P. Pivonka & D. Smith

Discipline of Civil, Surveying and Environmental Engineering, School of Engineering, The University of Newcastle, University Drive, Callaghan NSW 2308, Australia

C. Hellmich

Institute for Strength of Materials, Vienna University of Technology, Karlsplatz 13/202, A-1040 Vienna, Austria

ABSTRACT: For estimation of the durability of structures, it is highly desirable to quantify and simulate the chloride diffusion process in concrete. To this end, diffusion-cell experiments delivering the chloride diffusivity of cement pastes with different water-cement ratios (related to different microporosities) are evaluated in a scale-transition analysis. For prediction of the apparent chloride diffusivity, cement paste can be modelled by means of a differential scheme involving non-diffusive spherical inclusions in a diffusive matrix. As a result, chloride diffusivity of cement paste is obtained as a function of the microporosity and the chloride diffusivity in the micropore solution. Remarkably, the latter turns out to be one order of magnitude smaller than the chloride diffusivity in a pure salt solution system. The smaller diffusivity is probably caused by structuring of water molecules along the pore surface of cement paste.

Keywords: chloride-diffusion . cement paste. molecular water structuring. scale transition

1 INTRODUCTION

One of the most severe durability problems in civil engineering is the deterioration of reinforced concrete structures through corrosion of the reinforcing steel. This process is accelerated by the possible presence of chloride which may be transported from the concrete surfaces (where it typically occurs as part of sea water or deicing salts on bridges) to the reinforcing steel. Thereby, chloride can be transported either together with water through the micropore space, driven by differences in the pore water pressure (advective transport), or chloride can diffuse through the pore water, driven by differences in the chloride concentration. Herein, we focus on the second form of transport. For estimation of the durability of structures, it is highly desirable to quantify and simulate this diffusion process. However, the chloride diffusivity through concrete and cement paste is characterized by a large variation, which depends strongly on the water/cement ratio (Page et al., 1981), (Yu & Page, 1991), (Ngala et al., 1995), (Tang & Nilson, 1992), (MacDonald & Northwood, 1995). Explanations for this large variation and its chemo-physical origin are still a matter of debate. The possible significance of an electric (diffuse) double layer on the one hand

(Zhang & Gjørv, 1995), (Zhang & Buenfeld, 1997), (Chatterji, 1998), and of multispecies ionic transport on the other (Samson et al., 1999), (Samson & Marchand, 1999), (Truc et al., 2000), have been discussed, but no commonly accepted view has been established so far.

In this paper, we want to contribute to an explanation for the variation and the magnitude of chloride diffusivity in cement pastes. We evaluate numerous experimental data from cell-diffusion tests published in the open literature (Page et al., 1981), (Yu & Page, 1991), (Ngala et al., 1995), (Tang & Nilson, 1992), (MacDonald & Northwood, 1995), (Castellote et al., 2001), (Hornain et al., 1995), in the framework of a scale-transition analysis (Sen et al., 1981), (Dormieux & Lemarchand, 2001) between the micropore-space scale and the cement-paste scale.

2 DIFFUSION-CELL EXPERIMENTS FOR DETERMINATION OF CHLORIDE DIFFUSIVITY OF CEMENT PASTES

Steady-state chloride diffusion through water-saturated concrete and cement pastes is usually described by Fick's first law (Page et al., 1981),

(Yu & Page, 1991), (Ngala et al., 1995), (Tang & Nilson, 1992), (MacDonald & Northwood, 1995), (Hornain et al., 1995), (Castellote et al., 2001), e.g. in the form (Cussler, 1997):

$$\mathbf{J}_{paste} = -\mathbf{D}_{paste} \cdot \nabla c_{paste}, \quad (1)$$

where \mathbf{J}_{paste} , \mathbf{D}_{paste} , and ∇c_{paste} are the molar flux, the second-order diffusivity tensor, and the concentration gradient of sodium chloride in cement paste. Cement paste can be considered as isotropic material, $\mathbf{D}_{paste} = \mathbf{1}D_{paste}$, with the diffusion coefficient D_{paste} and the second-order unity tensor $\mathbf{1}$. D_{paste} is commonly determined by diffusion-cell tests, where two cells, filled with solutions characterized by different salt concentrations, are separated by a cylindrical cement paste sample with cross-sectional area A_{sample} and thickness t_{sample} (Figure 1(a)).

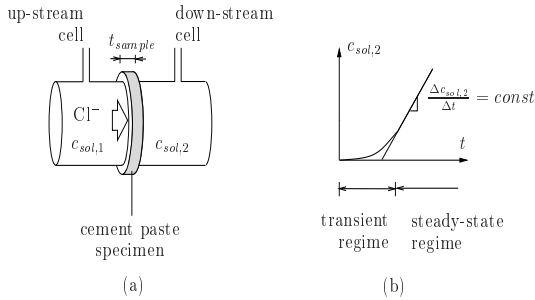


Figure 1. Diffusion cell test: (a) schematical sketch; (b) time-dependent evolution of chloride concentration in down-stream cell

The concentration in the upstream (source) compartment, $c_{sol,1}$ is kept constant during the experiment. Also, $c_{sol,1}$ is chosen much larger than the salt concentration in the downstream (collector) compartment, $c_{sol,2}$, i.e., $c_{sol,1} \gg c_{sol,2}$. At the beginning of the test (see Figure 1(b)) $c_{sol,2}$ is chosen to be virtually zero. The chloride ions need a certain time span to move into the downstream compartment. The end of this time span is indicated by an increase of $c_{sol,2}$ in the downstream compartment (see Figure 1(b)). The chloride concentrations adjacent to the circular surfaces of the cement paste sample, $c_{paste,i}$, $i = 1, 2$, can be determined from the chloride concentrations in the solutions of the up-stream and the down-stream cell, $c_{sol,i}$, $i = 1, 2$, and from the microporosity ϕ of the cement paste sample, through

$$c_{paste,i} = \phi \cdot c_{sol,i} \quad \text{with } i = 1, 2. \quad (2)$$

Thus, monitoring change of $c_{sol,2}$ over time intervals Δt allows for estimation of the chloride flux,

$$J_{paste} = \frac{V_{cell,2}}{A_{sample}} \frac{\Delta c_{paste,2}}{\Delta t}, \quad (3)$$

where $V_{cell,2}$ denotes the volume of the down-stream cell. First, $\Delta c_{sol,2} / \Delta t$ is changing (Figure 1(b)), so that transient conditions prevail. The duration of transient conditions increases with increasing thickness of the specimen. Afterwards, steady state conditions (i.e., $\Delta c_{sol,2} / \Delta t = const$), are observed. They allow for estimation of the chloride diffusion coefficient, based on the discrete 1D specification of Fick's first law for the diffusion-cell test,

$$J_{paste} = -D_{paste} \cdot \frac{\Delta c_{paste}}{\Delta x} = -D_{paste} \cdot \frac{c_{paste,2} - c_{paste,1}}{t_{sample}} \quad (4)$$

D_{paste} can be expressed from Eqn. (4) and Eqn. (3), in the form:

$$D_{paste} = \frac{V_{cell,2} \Delta c_{paste,2}}{A_{sample} \Delta t} \frac{t_{sample}}{c_{paste,1} - c_{paste,2}}. \quad (5)$$

Insertion of Eqn. (2) into (5) provides a relation for the determination of the diffusion coefficient of cement pastes from the physical properties accessible in diffusion-cell tests:

$$D_{paste} = \frac{V_{cell,2} \Delta c_{sol,2}}{A_{sample} \Delta t} \frac{t_{sample}}{c_{sol,1} - c_{sol,2}}, \quad (6)$$

D_{paste} is commonly referred to as 'apparent diffusion coefficient' of cement paste (Page et al., 1981), (MacDonald & Northwood, 1995), (Castellote et al., 2001), or more properly, as mass transfer coefficient (Cussler, 1997).

Diffusion-cell tests are typically performed in order to explore the effects of variations of (i) the water/cement ratio (Page et al., 1981), (MacDonald & Northwood, 1995), (ii) the curing conditions (Dehghanian & Arjemandi, 1997), (Ampadu et al., 1999), and (iii) the sodium chloride concentration (Page et al., 1981), (MacDonald & Northwood, 1995), (Figure 2; for a more detailed discussion on boundary and curing conditions used for the cement paste diffusion experiments see Pivonka et al., (2003)).

Whereas the influence of different curing conditions and of the sodium chloride concentration turns out to be of secondary importance, the strong functional dependence between water-cement ratio (w/c) and apparent diffusion coefficient D_{paste} is striking (Figure 2). The chemo-physical origin of this dependence will be elucidated next, by performance and interpretation of a scale-transition analysis.

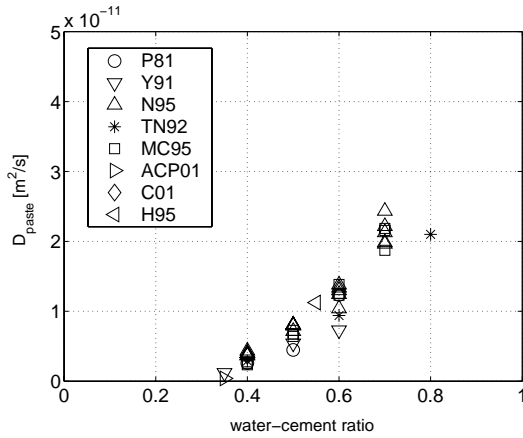


Figure 2. Dependence of chloride diffusion coefficients of cement paste D_{paste} on w/c-ratio (YU91: (Yu & Page, 1991), N95: (Ngala et al., 1995), TN92: (Tang & Nilson, 1992), MC95: (MacDonald & Nothwood, 1995), ACP01: (Asbridge et al., 2001), C01: (Castellote et al., 2001), H95: (Hornain et al., 1995)).

3 EVALUATION OF EXPERIMENTS BY A SCALE-TRANSITION ANALYSIS

In cement paste, the diffusive transport of chloride ions takes place in the micropores (Buenfeld et al., 1998) as long as they percolate, i.e. as long as they form a continuous pathway (Garboczi & Bentz, 1992). This is the common situation to which we refer herein. The rather large ratio of micropore diameter (1-100 microns) to the diameter of the ions (400 pm) encountered in cement paste allows for a continuum description of diffusive transport of chloride through the (saturated) pores.

We consider cement paste as a porous medium defined on a representative volume element (RVE) of some millimeters characteristic length l (Figure 3).

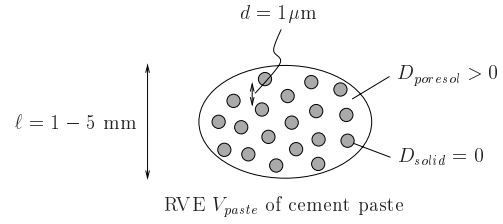


Figure 3. Representation of cement paste as a two phase material

This medium consists of two phases, schematically indicated in Figure 3, a sodium-chloride-solution filled micropore space and a solid phase consisting of aluminosilicate hydrates. While the solid phase is regarded as non-diffusive ($D_{solid} \equiv 0$), we assign an average diffusion coefficient $D_{poresol}$ to the pore fluid containing sodium chloride, presuming at this point the validity of Fick's first law in the micropore space

$$\mathbf{j}_{poresol} = -D_{poresol} \cdot \nabla c_{poresol} \quad (7)$$

This equation holds at the length scale of the micropores, for characteristic size $d \ll l$. At this scale, we are not aware of any measurement techniques for the estimation of $D_{poresol}$. As a first guess (the validity of which will be discussed later), $D_{poresol}$ may be assumed to match the sodium chloride diffusion coefficient of a pure solution system, i.e., $D_{poresol} = 1.61 \cdot 10^{-9} m^2/s$ (Robinson & Stokes, 1959), see also Tables 1 and 2.

A micro-macro transition law relating $D_{poresol}$ and \mathbf{D}_{paste} is standardly given in the form (Bear & Bachmat, 1991), (Dormieux & Lemarchand, 2001) (pp 1268, Equation (9))

$$\mathbf{D}_{paste} = \phi D_{poresol} \mathbf{T}, \quad (8)$$

where $\phi = V_{pore} / V_{paste}$ is the microporosity of cement paste (V_{pore} is the volume of micropores in the RVE with volume V_{paste}); and \mathbf{T} is the second order 'tortuosity tensor', capturing geometrical information about the pore shape and arrangement (pore morphology). Accounting for the anisotropy of the material, $\mathbf{D}_{paste} = \mathbf{1} D_{paste}$, Eqn. (8) can be recast in the simpler form

$$D_{paste} = \phi D_{poresol} T, \quad (9)$$

with the (dimensionless) tortuosity factor T .

Without any further knowledge about the pore space except its porosity ϕ and its isotropic nature, the tortuosity tensor \mathbf{T} can be suitably estimated using the so-called differential scheme of continuum micromechanics (Zaoui, 1997), (Dormieux & Lemarchand, 2001), (Lemarchand, 2001). Based on Eshelby's 1957 matrix inclusion problem (Eshelby, 1957), an infinitesimal amount of solid spherical inclusions is introduced into a matrix with $D_{poresol}$. The solid-fluid mixture is homogenized into a material with a well-defined diffusivity. This material serves as the matrix for the next infinitesimal amount of solid inclusions. This procedure is repeated until the actual solid volume fraction ($1-\phi$) is reached, leading to the result (Dormieux & Lemarchand, 2001)

$$\mathbf{T} = \phi^{1/2} \mathbf{1}, \quad (11)$$

$$\mathbf{D}_{paste} = \phi^{3/2} D_{poresol} \mathbf{1} \rightarrow D_{paste} = \phi^{3/2} D_{poresol}. \quad (12)$$

Exactly the same result can be achieved by a differential effective medium approach for an assemblage of perfectly spherical grains (Sen et al., 1981).

Having thus gained confidence in the relevance of the micro-macro transition law Eqn. (12), we want to confront this relation to experimental data. This requires determination of the water-saturated microporosity ϕ from experiments.

Acker, (2001) has given the composition of cement pastes as a function of the water-cement ratio and the degree of hydration ξ (Figure 4), reading as

$$\bar{V}_{cem}(\xi) = 1 - \xi, \quad (13)$$

$$\bar{V}_{H_2O}(\xi) = \frac{\rho_{cem}}{\rho_{H_2O}} \langle w/c - 0.42 \xi \rangle, \quad (14)$$

$$\bar{V}_{hyd}(\xi) = \frac{\rho_{cem}}{\rho_{hyd}} \xi, \quad (15)$$

Here, $\langle \cdot \rangle$ represents the McAuley brackets, $\langle x \rangle = 1/2(x + |x|)$. $\rho_{cem} = 3.15 \text{ kg/dm}^3$, $\rho_{H_2O} = 1.0 \text{ kg/dm}^3$, and $\rho_{hyd} = 1.46 \text{ kg/dm}^3$ (Acker, 2001) are the real mass densities of cement, water, and hydrates. \bar{V}_i stands for the volume of component i normalized with respect to the volume of cement at $\xi = 0$ (i.e. at the beginning of the hydration);

$$\bar{V}_i(\xi) = V_i / V_{cem}(\xi = 0) \rightarrow \bar{V}_{cem}(\xi = 0) = 1, \quad (16)$$

see also Figure 4.

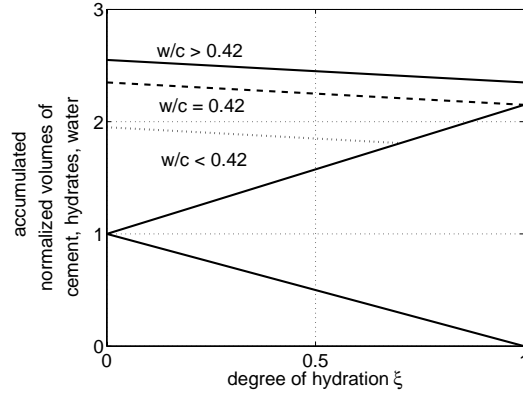


Figure 4. Volumes of cement paste components as a function of the degree of hydration, estimated according to Acker (2001)

For $w/c < 1$, lack of water causes that part of the cement remains unhydrated ($\xi_{\infty} < 1$), see dotted line in Figure 4. However, all considered pastes with initial water-cement ratio $(w/c)_i < 0.42$ (Figure 2 and 4) were cured in water baths for at least 28 days (see Pivonka et al., (2003) for details), so that they most probably attained a water-cement ratio of $(w/c)_c = 0.42$ during curing. The duration of the curing period of all considered pastes, ranging between 28 and 270 days, also suggests a complete hydration of the pastes at the end of the curing time, $\xi_{\infty} = 1$. Furthermore, water curing implies the filling of all original air pores (occupying normalized volume \bar{V}_{air}) with water. This renders the volume fraction of the water-saturated micropores (or porosity ϕ) as the following function of the water-cement ratio:

$$\phi(w/c) = \frac{\bar{V}_{air}(\xi = 1, w/c \geq 0.42) + \bar{V}_{H_2O}(\xi = 1, w/c \geq 0.42)}{[\bar{V}_{air} + \bar{V}_{H_2O} + \bar{V}_{hyd} + \bar{V}_{cem}](\xi = 1, w/c \geq 0.42)} \quad (17)$$

where we make use of the relationships Eqn. (13) to Eqn. (15). Respective porosity values for the data base depicted in Figure 2 range between 7% and 38% (see Figure 5).

Experimentally determined data pairs (ϕ, D_{paste}) , are largely overestimated by the theoretical relationship Eqn. (12) if $D_{poresol} = 1.61 \cdot 10^{-9} \text{ m}^2/\text{s}$ is assumed (see thin line in Figure 5). In other words, the simple guess of setting the pore solution diffusivity equal to the salt diffusivity in a pure

solution system, $D_{NaCl} = 1.61 \cdot 10^{-9} \text{ m}^2/\text{s}$ turns out to be wrong.

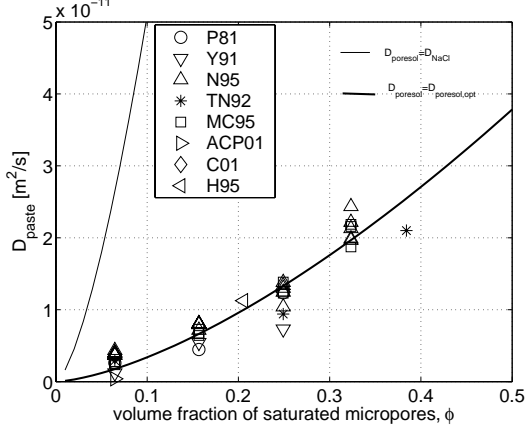


Figure 5. Chloride diffusivity as a function of water-saturated porosity: Comparison of experimental data and diffusion coefficients obtained by means of homogenization, Eqn. (12) with $D_{poresol} = D_{NaCl} = 1.61 \cdot 10^{-9} \text{ m}^2/\text{s}$ (thin line) and $D_{poresol} = D_{poresol,opt} = 1.07 \cdot 10^{-10} \text{ m}^2/\text{s}$ (thick line)

However, what can also be seen is that the trend of the theoretical relationship fits very well with the one of the experiments. In fact, using a pore diffusion coefficient $D_{poresol} = 1.07 \cdot 10^{-10} \text{ m}^2/\text{s}$, we get an excellent representation of the experimental data by Eqn.(12) ($r^2 = 0.92$). This is an extraordinary correlation given the simplicity of the micro-macro transition law and of the relation for the estimation of the water-saturated porosity Eqn. (17). $D_{poresol,opt}$ was determined by minimizing the mean relative error between ($n = 28$) experimental values $D_{paste,i}$ and homogenization results $D_{paste}(\phi_i)$ from Eqn. (12), (see Pivonka et al., (2003) for details)

$$\bar{\epsilon} = \frac{1}{n} \sum \frac{D_{paste,i} - (\phi_i)^{3/2} D_{poresol}}{D_{paste,i}} \rightarrow \text{Min} \quad (18)$$

$$\Rightarrow D_{poresol,opt}$$

The surprising result is that the various experimental data could be reproduced well using a single diffusion coefficient, i.e., $D_{poresol,opt}$ of the pore solution. The question now raised is, why the pore diffusion coefficient, $D_{poresol,opt}$, differs from the sodium chloride diffusion coefficient D_{NaCl} by a factor of 1/15.

4 DISCUSSION OF CHLORIDE DIFFUSION IN THE MICROPORE SPACE OF CEMENT PASTES

In order to suggest a reasonable explanation for the magnitude of the pore-space diffusion coefficient $D_{poresol,opt}$ we determined previously, we have to precisely define the physical meaning of the diffusion coefficients D_{paste} (Eqn. (1)) and $D_{poresol}$ (Eqn. (7)). For this reason, we give a short review of diffusive transport in pure liquids and charged porous media.

In a system consisting exclusively of a solution (pure solution system), four types of diffusion are commonly distinguished (Shackelford & Daniel, 1991a) (see Figure 6): (i) self-diffusion, (ii) tracer diffusion, (iii) salt diffusion, and (iv) counter diffusion.

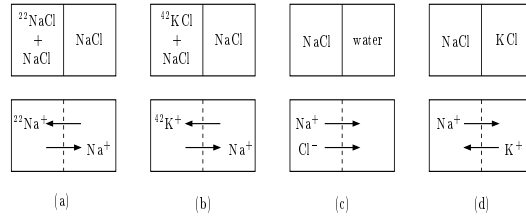


Figure 6. Different types of diffusion: (a) self-diffusion, (b) tracer-diffusion, (c) salt diffusion, and (d) counter diffusion (according to Shackelford & Daniel, (1991))

In case of dilute binary mixtures (one solute and one solvent), the first two types of diffusion (self-diffusion and tracer diffusion) can be described by Fick's first law (Cussler, 1997):

$$\mathbf{J}_i = -D_i \nabla c_i, \quad (19)$$

where \mathbf{J}_i denotes the molar flux density, D_i is the diffusion coefficient of the ion, and c_i is the concentration of ionic species i . Self-diffusion coefficients for anions and cations in infinitely dilute solutions (Table 1) are computed from the Einstein relation, i.e. from $D_i = RTu_i$, where the experimental values for the mobility u_i are extrapolated to zero concentrations.

For the description of salt diffusion, i.e. of diffusion of dilute binary electrolytes (2 (charged) solutes and 1 solvent), the Nernst-Planck (N-P) equation is required (Newman, 1991), reading for individual ions as:

$$\mathbf{J}_i = -D_i (\nabla c_i + \frac{F}{RT} z_i c_i \nabla \psi), \quad (20)$$

where F is the Faraday constant, z_i and D_i are the charge number and the self-diffusion coefficient of the i -th ion, R is the universal gas constant, T is the absolute temperature, ψ is the electric potential. The N-P equation (20) expresses that the ionic species i may be driven by a gradient of the electric field $-\nabla \psi$ (migration) and/or by an ionic concentration gradient $-\nabla c_i$ (diffusion). In the absence of net current flow (electroneutrality), the gradient of the electric potential can be expressed as (Newman, 1991):

$$\nabla \psi = -\frac{RT}{F} \frac{D_+ - D_-}{z_+ D_+ - z_- D_-} \frac{1}{c_{sol}} \nabla c_{sol}. \quad (21)$$

with the salt concentration $c_{sol} = c_+ / \nu_+ = c_- / \nu_-$ where the subscripts \pm indicate cations and anions, respectively; and ν_+ and ν_- are the stoichiometric coefficients. Integration of Eqn. (21) leads to the diffusion potential (liquid junction potential) for a binary electrolyte, reading as:

$$\Delta \psi_L = -\frac{RT}{F} \frac{D_+ - D_-}{z_+ D_+ - z_- D_-} \ln \left(\frac{c_{sol,2}}{c_{sol,1}} \right). \quad (22)$$

Insertion of Eqn. (21) into the N-P-equation (20) delivers a steady-state diffusion equation for salts;

$$\mathbf{J}_{sol} = -D_{sol} \nabla c_{sol}, \quad (23)$$

where \mathbf{J}_{sol} and c_{sol} are the molar flux density and the concentration of the respective salt; and the salt diffusion coefficient D_{sol} has the form:

$$D_{sol} = \frac{D_+ D_- (z_+ - z_-)}{z_+ D_+ - z_- D_-} \quad (24)$$

see Table 1. The mathematical similarity between Eqn. (23) and Eqn. (19) indicates that a salt solved in water behaves like a single ionic species, because of the electroneutrality requirement. In more detail, different self-diffusion coefficients of the anion and cation result in separation of the species. This leads to creation of a minute dipole density which then prevents further separation. The dipole density creates a potential (diffusion potential, Eqn. (22)) which acts to speed up the ion with the smaller self-diffusion coefficients and slow down the ion with the larger self-diffusion coefficient. Experiments show a dependence of salt diffusion coefficients on different concentrations (see Table 2). However, the diffusion coefficients

of concentrated solutions (Table 2) and dilute solutions (Table 1) reasonably agree for concentrations up to 3.0 mol/L as far as NaCl and KCl solutions are concerned, and up to 1.0 mol/L for HCl solutions. Since we considered in our scale-transition analysis non-dilute concentrations in the micropore solution, which are smaller than 3 mol/L, the use of Fick's law Eqn. (7) for the description of diffusive transport in the micropore space of cement paste is justified.

Table 1. Salt diffusion (1:1 electrolytes, i.e., $z_+ = +1$, $z_- = -1$) and self-diffusion coefficients (infinite dilute solution, according to Robinson & Stokes, (1959))

electrolyte	D_{sol}	D_+	D_- [$10^{-9} \text{m}^2/\text{s}$]
HCl	3.336	9.31	2.03
NaCl	1.610	1.33	2.03
KCl	1.994	1.96	2.03

Table 2. Salt diffusion coefficients at various concentrations at 25°C (according to Robinson & Stokes, (1959))

c [mol/L]	NaCl	KCl	HCl
0.05	1.51	1.86	3.07
0.1	1.48	1.84	3.05
0.5	1.47	1.85	3.18
1.0	1.48	1.89	3.43
3.0	1.57	2.11	4.65

Still, with respect to pure solution systems, additional phenomena affect the diffusive transport in the micropores of cement, reducing the drift speed of chloride. The decrease of ionic drift speed in the pores may be attributed to: (i) the presence of an (electrical) diffuse-double layer (DDL) on particle surfaces, (ii) the presence of high concentrations of multiple ions in the pore solution, and (iii) changes of the viscosity of the pore solution caused by structuring of water. Let us more profoundly discuss these three possibilities:

(i) Zeta potential measurements of cement pastes (Nägele, 1985), (Nägele, 1989) indicate negative surface charges on cement paste particles. The region where 'counterions' balance this excess charge is generally called electrical diffuse-double layer (DDL) (Revil, 1999). It may be described by double- or triple layer models (see, e.g., (Hiemenz & Rajagopalan, 1997)). However, the presence of a DDL has been shown to *increase* (rather than decrease) the salt diffusivity (Revil, 1999). Consequently, the retardation of chloride ions cannot be attributed to the DDL. The DDL

seemingly does not have an discernible effect on the chloride diffusivity of cement pastes at all, probably because of its compression due to salt concentrations around 1 mol/L NaCl, as was shown for a charged porous medium (Pivonka & Smith, 2003).

(ii) Experimental investigations of the cement pore solution have shown that the pore solution consists of multiple ions such as Na^+ , K^+ , Ca^{2+} , OH^- , and SO_4^{2-} ions (Diamond, 1981), (Andrade, 1993) (Zhang & Gjrv, 1994), (Buenfeld et al., 1998), (Chatterji, 1999). While in this case the ionic flux of each species can still be quantified by the N-P Eqn. (20), the electric potential does not follow any more from Eqn. (22), but from the more complex Henderson formula (Helfferich, 1962)

$$\Delta\psi_L = -\frac{RT}{F} \frac{\sum_{i=1}^N z_i D_i (c_{i,2} - c_{i,1})}{\sum_{i=1}^N z_i^2 D_i (c_{i,2} - c_{i,1})} \ln \left(\frac{\sum_{i=1}^N z_i^2 c_{i,2}}{\sum_{i=1}^N z_i^2 c_{i,1}} \right) \quad (25)$$

This formula allows for quantification of the effect of multiple ions on the chloride diffusivity. E.g. for a NaCl concentration ratio of $c_{sol,2} / c_{sol,1} = 10$, addition of ions such as Na^+ , K^+ , and OH^- , in concentrations 150, 400, 550 mol/m³ to a 1 molar NaCl-solution, resulting in a multi-species solution typical for cement pastes (Truc et al., 2000), leads to a decrease of the (absolute value of) the diffusion potential from $\psi_L = -13$ mV (for the NaCl solution Eq. (22)) to $\psi_L = -3$ mV (for the multispecies solution Eq. (25); the diffusion potential is chosen as zero at the up-stream side of the sample). This decrease and specification of the N-P Eqn.(20) for chloride, $z_{cl} = -1$, show that the presence of Na^+ , K^+ , and OH^- lead to an *acceleration* (rather than to a retardation) of the chloride drift speed. Hence, judging from the diffusion potential, the decrease of chloride diffusivity in the saturated micropore space of cement pastes cannot be attributed to the presence of multiple ionic species.

A second characteristic of multispecies solutions is the smaller distance between ions, increasing the importance of ion-ion interactions. The presence of high concentrations of multiple ions in solution is standardly taken into account using activity coefficients (Atkins & dePaula, 2002) which describe the deviation of a solution from ideality. There are several theories for describing the

relationship between activity coefficient and ionic concentration (strength) of the solution. Among these the Pitzer model (Pitzer, 1973) and the extended Debye-Hckel model (Kunze, 1986) are most commonly applied. However, application of the latter model for salt concentrations up to 1 mol/L at the pure solution level showed only a small variation of the salt diffusion coefficient, typically between 4 % (for NaCl and KCl solution) and 8 % (for LiCl solution, see Tang, (1999b) for details). Hence, the influence of additional ions in a multi-species solution seems inappropriate to explain the decrease of salt diffusivity in the micropores of cement pastes by the factor 1/15. This is in agreement with the numerical simulations of multi-species diffusion conducted in Truc et al., (2000).

(iii) Evidence has been put forward for almost one century that charged surfaces may imply structuring or layering of water, see (Pollack, 2001) for a historical review. This phenomenon is known to occur in numerous materials, including e.g. biopolymers (Israelachvili & Wennerstrm., 1996). In more detail, the polar nature of the water molecules leads to their absorption at the charged surfaces, constituting a first layer. Then, additional layers adhere one upon the other, forming a multilayered network. This layered network has physical properties which are distinctively different from standard liquid water; e.g. the viscosity of layered water is significantly higher. Molecular dynamic (MD) simulations of a clay - salt water system show that the salt diffusion coefficient strongly depends on the viscosity of the pore solution (Ichikawa et al., 2000), (Ichikawa et al., 2002). While a viscosity of $\mu_w = 0.001$ kg/(m s) leads to a diffusion coefficient of $D_{sol} \approx 1.7 \cdot 10^{-9}$ m²/s, which is close to the one for a NaCl solution ($D_{sol} \approx 1.61 \cdot 10^{-9}$ m²/s, see Table 1), an increase of viscosity to $\mu_w = 0.007$ kg/(m s) leads to a diffusion coefficient of $D_{sol} \approx 2.5 \cdot 10^{-10}$ m²/s. The latter value is of the same order of magnitude as the chloride diffusivity we determined for the pore solution of cement paste ($D_{poresol,opt} = 1.1 \cdot 10^{-10}$ m²/s). The viscosity increase (and the diffusivity decrease, respectively) can be detected over a distance as large as several hundred nanometers (Szent-Gyrgyi, 1972).

The 'spiny structure' of cement paste at complete hydration (Figure 7) (Ashby & Jones, 1994)

exhibits features of exactly this characteristic length.

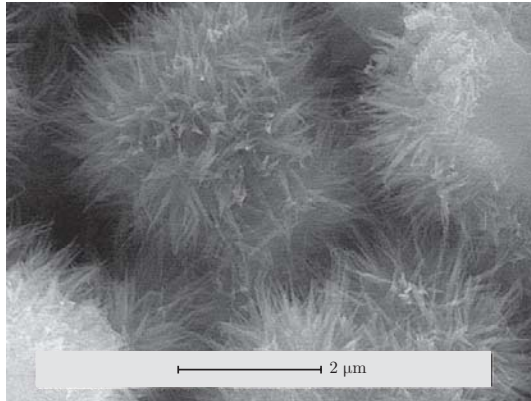


Figure 7. Morphology of the cement paste microstructure obtained from environmental scanning electron microscope (ESEM), 28 days after the onset of hydration (according to Tritthart & Häussler, (2003))

This renders structuring of water as the prime candidate for the explanation of the decrease of chloride diffusivity in the micropore space of cement paste with respect to a pure salt solution.

5 CONCLUSIONS

For prediction of the apparent chloride diffusivity, cement paste can be modelled by means of a differential scheme involving non-diffusive spherical inclusions in a diffusive matrix. As a result, chloride diffusivity of cement paste is obtained as a function of the microporosity and the chloride diffusivity in the micropore solution. Remarkably, the latter turns out to be one order of magnitude smaller than the chloride diffusivity in a pure salt solution system. The smaller diffusivity is probably caused by a higher viscosity of the pore solution. This higher viscosity can be explained by the structuring of water molecules along the charged pore surfaces, a well-known phenomenon in clays and biological materials.

6 ACKNOWLEDGEMENT

The first author gratefully acknowledge the financial support of this study by the 'Austrian Foundation for the Promotion of Scientific Research (FWF)' in the course of an Erwin Schrödinger scholarship.

7 REFERENCES

- P. Acker, 2001. Micromechanical analysis of creep and shrinkage mechanisms, in: F. J. Ulm, Z. Bažant, F. Wittmann (Eds.), *Creep, Shrinkage, and Durability of concrete and other Quasi-brittle Material - Proceedings of the Sixth International Conference CONCREEP-6@MIT*, Elsevier, Amsterdam, pp. 15-26.
- K. Ampadu, K. Torii, M. Kawamura, 1999. Beneficial effect of fly ash on chloride diffusivity of hardened cement paste, *Cement and Concrete Research* 29, 585-590.
- C. Andrade, 1993. Calculation of chloride diffusion coefficients in concrete from ionic migration measurements, *Cement and Concrete Research* 23, 724-742.
- A. Asbridge, G. Chadborn, C. Page, 2001. Effects of metakaolin and the interfacial transition zone on the diffusion of chloride ions through cement mortars, *Cement and Concrete Research* 31, 1567-1572.
- M. Ashby, D. Jones, 1994. *Engineering Materials 2*, Elsevier Science Inc, New York, USA.
- P. Atkins, J. dePaula, 2002. *Atkins' physical chemistry*, 7th Edition, Oxford University Press, New York, USA .
- J. Bear, Y. Bachmat, 1991. *Introduction to modelling of transport phenomena in porous media, Vol.-4*, Kluwer Academic Publishers, Dordrecht, Netherlands.
- N. Buenfeld, G. Glass, A. Hassanein, J.-Z. Zhang, 1998. Chloride transport in concrete subjected to electric field, *ASCE Journal of Materials for Civil Engineering* 10(4), 220-28.
- M. Castellote, C. Alonso, C. Andrade, G. Chadborn, C. Page, 2001a Oxygen and chloride diffusion in cement pastes as a validation of chloride diffusion coefficients obtained by steady-state migration tests, *Cement and Concrete Research* 31, 621-625.
- M. Castellote, C. Andrade, C. Alonso, 2001b Measurement of steady and non-steady-state chloride diffusion coefficients in a migration test by means of monitoring the conductivity in the anolyte chamber. Comparison with natural diffusion tests, *Cement and Concrete Research* 31(10), 1411-1420.
- S. Chatterji, 1998. Colloid electrochemistry of saturated cement paste and some properties of cement based materials, *Advanced Cement Based Materials* 7, 102-108.
- S. Chatterji, 1999. Evidence of variable diffusivity of ions in saturated cementitious materials, *Cement and Concrete Research* 29, 995-998, communication .
- E. Cussler, 1997. *Diffusion mass transfer in fluid systems*, 2nd Edition, Cambridge University Press, New York, USA.
- C. Dehghanian, M. Arjemandi, 1997. Influence of slag blended cement concrete on chloride diffusion rate, *Cement and Concrete Research* 27(6) 937-945.
- S. Diamond, 1981. Effects of two Danish fly ashes on alkali contents of pore solutions of cement - fly ash pastes, *Cement and Concrete Research* 11, 383-394.
- L. Dormieux, E. Lemarchand, 2001. Homogenization approach of advection and diffusion in cracked porous media, *ASCE Journal of Engineering Mechanics* 127(12), 1267-1274.
- J. D. Eshelby, 1957. The determination of the elastic field of an ellipsoidal inclusion, and related problems, *Proceedings of the Royal Society of London A241 (1226)*, 376-396.
- E. Garboczi, D. Bentz, 1992. Computer simulation of the diffusivity of cement based materials, *Journal of Material Science* 27, 2083-2092.
- F. Helfferich, 1962. *Ion exchange*, McGraw-Hill, New York, USA .
- P. Hiemenz, R. Rajagopalan, 1997. *Principles of colloid and surface chemistry*, 3rd Edition, Marcel Dekker, New York, USA.

- H. Hornain, J. Marchand, V. Duhot, M. Moranville-Regourd, 1995. Diffusion of chloride ions in limestone filler blended cement pastes and mortars, *Cement and Concrete Research* 25(8), 1667-1678.
- Y. Ichikawa, K. Kawamura, M. Nakano, K. Kitayama, N. Fujii, 2000. Molecular behavior and micro/macro analysis of diffusion problem in bentonite, in: CD-ROM Proceedings of the European Congress on Computational Methods in Applied Sciences and Engineering, Barcelona, Spain.
- Y. Ichikawa, K. Kawamura, N. Fujii, T. Nattavut, 2002. Molecular dynamics and multiscale homogenization analysis of seepage/diffusion problem in bentonite clay, *International Journal for Numerical Methods in Engineering* 54, 1717-1749.
- J. Israellachvili, H. Wennerström, 1996. Role of hydration and water structure in biological and colloidal interactions, *Nature* 379, 219—225.
- U. Kunze, 1986. *Grundlagen der quantitativen Analyse*, 2nd Edition, Georg Thieme, Stuttgart, Germany .
- E. Lemarchand, 2001. Contribution de la micromécanique à l'étude des phénomènes de transport et couplage poromécanique dans les milieux poreux: {A}pplication aux phénomènes de gonflement dans les géomatériaux, Ph.D. thesis, Ecole Nationale des Ponts et Chaussées, Paris, France.
- K. MacDonald, D. Northwood, 1995. Experimental measurements of chloride ion diffusion rates using a two-compartment diffusion cell: effects of material and testvariables, *Cement and Concrete Research* 25(7) , 1407-1416.
- E. Nägele, 1985. The zeta potential of cement, *Cement and Concrete Research* 15 (453).
- E. Nägele, 1989. The transient zeta potential of hydrating cement, *Chemical engineering science* 44(8), 1637-1645.
- J. Newman, 1991. *Electrochemical Systems*, 2nd Edition, Prentice-Hall, Englewood Cliffs, NJ, USA.
- V. Ngala, C. Page, L. Parrott, S. Yu, 1995. Diffusion in cementitious materials: 2. further investigations of chloride and oxygen diffusion in well-cured OPC and OPC/20%PFA pastes, *Cement and Concrete Research* 25(4), 819-826.
- C. Page, N. Short, A. Tarras, 1981. Diffusion of chloride ions in hardened cement pastes, *Cement and Concrete Research* 11 (3) , 395-406.
- K. Pitzer, 1973. Thermodynamics of electrolytes I. theoretical basis and general equations, *The Journal of Physical Chemistry* 77(2), 268-277.
- P. Pivonka, C. Hellmich, D. Smith, 2003. Is chloride diffusivity of cement pastes mainly governed by paste-specific microporosity and paste independent molecular structuring of micropore water ? - arguments from a scale transition analysis, *Cement and Concrete Research*, submitted for publication.
- P. Pivonka, D. Smith, 2003. Fundamental theoretical study of nanoscale ion transport through charged porous rocks: Part 1- diffusion, 9th Australia New Zealand Conference on Geomechanics.
- G. Pollack, 2001. *Cells, gels and the engines of life: a new unifying approach to cell function*, Ebner and Sons, Seattle Washington, USA.
- A. Revil, 1999. Ionic diffusivity, electrical conductivity, membrane and thermoelectric potentials in colloids and granular porous media: a unified model, *Journal of Colloid and Interface Science* 212 , 503-522.
- R. Robinson, R. Stokes, 1959. *Electrolyte solutions*, 2nd Edition, Butterworths Scientific Publications, London, England.
- E. Samson, J. Marchand, 1999. Numerical solution of the extended Nernst-Planck model, *Journal of Colloid and Interface Science* 215, 1-8.
- E. Samson, G. Lemaire, J. Marchand, J. Beaudoin, 1999. Modeling chemical activity effects in strong ionic solutions, *Computational Material Science* 15, 285-294.
- P. Sen, C. Scala, M. Cohen, 1981. A self-similar model for sedimentary rocks with application to the dielectric constant of fused glass beads, *Geophysics* 46(5) , 781-795.
- C. Shackelford, D. Daniel, 1991. Diffusion in saturated soil. {I}: background, *Geotechnical Engineering* 117(3), 467-484.
- J. Stark, B. Wicht, 2001. *Dauerhaftigkeit von Beton*, 2nd Edition, Birkhäuser Verlag, Basel, Schweiz .
- A. Szent-Györgyi, 1972. *The living state. With observations of cancer*, Academic Press, New York, USA.
- L. Tang, L.O. Nilson, 1992. Rapid determination of chloride diffusivity in concrete by applying an electrical field, *ACI Materials Journal* 89(1), 49-53.
- L. Tang, 1999a. Concentration dependence of diffusion and migration of chloride ions. part 1: theoretical considerations, *Cement and Concrete Research* 29, 1463-1468.
- L. Tang, 1999b. Concentration dependence of diffusion and migration of chloride ions. part 2: experimental evaluations, *Cement and Concrete Research* 29, 1469-1474.
- J. Tritthart, F. Häussler, 2003. Pore solution analysis of cement pastes and nanostructural investigations of hydrated C₃S , *Cement and Concrete Research* 33, 1063-1070.
- O. Truc, J. Ollivier, L. Nielsson, 2000. Numerical simulation of multi-species transport through saturated concrete during migration test - MsDiff code, *Cement and Concrete Research* 30, 1581-1592.
- S. Yu, C. Page, 1991. Diffusion in cementitious materials: 1. comparative study of chloride and oxygen diffusion in hydrated cement pastes, *Cement and Concrete Research* 21, 581-588.
- A. Zaoui, 1997. Structural morphology and constitutive behavior of micro-heterogeneous materials, in: P. Suquet (Ed.), *Continuum Micromechanics, CISM courses and lectures No. 377*, International Centre for Mechanical Science, Springer, New York, USA, pp. 291-347.
- T. Zhang, O. E. Gjörv, 1994. An electrochemical methode for accelerated testing of chloride diffusivity of concrete, *Cement and Concrete Research* 24(8), 1534-1548.
- T. Zhang, O. E. Gjörv, 1995. Effect of ionic interaction in migration testing of chloride diffusivity in concrete, *Cement and Concrete Research* 25(7) , 1535-1542.
- J.Z. Zhang, N. Buenfeld, 1997. Presence and possible implications of a membrane potential in concrete exposed to chloride solution, *Cement and Concrete Research* 27(6) , 853-859.