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Chloride ingress in cement paste and mortar

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Abstract

In this paper chloride ingress in cement paste and mortar is followed by electron probe microanalysis. The influence of several paste and exposure parameters on chloride ingress are examined (e.g., water-cement ratio, silica fume addition, exposure time, and temperature). The measurements are modelled on Fick's law modified by a term for chloride binding. Inclusion of chloride binding significantly improves the profile shape of the modelled ingress profiles. The presence of fine aggregate and formation of interfacial transition zones at paste-aggregate boundaries does not significantly affect diffusion rates.

Keywords: EDX; Diffusion; Chloride; High-performance concrete; EPMA

1. Introduction

Chloride ingress is a common cause of deterioration of reinforced concrete structures. Concrete may be exposed to chloride by seawater or deicing salts; chloride initiates corrosion of the reinforcement, which through expansion disrupts the concrete. Modelling the chloride ingress is an important basis for designing the durability of concrete structures. As an example the Danish Great Belt link is designed to have 100 years of durability based on calculation of chloride ingress [1].

During the last 15 years the types of concrete used in practice have changed substantially by increased use of plasticizers and mineral additives; concretes with higher strengths and reduced permeability result. Recently it has become clear that traditional chloride ingress models are not applicable to modern concretes.

Chloride ingress in modern concretes cannot be followed with conventional measuring techniques. This makes it difficult to test new models. However, previous experiments have shown that electron probe microanalysis (EPMA) is applicable for this purpose [2]. The geometric resolution for the EPMA method is 100–1000 times better than that of conventional techniques.

The present project aims to achieve a better understanding of the physical-chemical nature of chloride ingress. A number of different cement pastes and mortars were examined, ranging from traditional to modern high-performance types. The pastes and mortars were exposed to synthetic seawater from 1 day to half a year. Thereafter, the samples were examined by EPMA.

This paper is a condensed version of a report [3] where a more complete treatment can be found.

2. Methods

2.1. Summary of experiments

Approximately 50 different cement paste and mortar samples were made. The mixtures had silica fume additions in the range 0–20 wt% and water-cement (w/c) ratios between 0.2 and 0.7. After approximately 100 days of prehardening and water saturation, the samples were exposed to a 3% NaCl solution (synthetic seawater) for 1 to 180 days at temperatures of 4, 20, and 35°C; these are termed "leaching conditions." In addition to these parameters, the influence of mixing technique and addition of superplasticizer were examined. For some pastes simulated pore fluids were prepared to minimize leaching during chloride exposure. This was done by equilibrating crushed cement paste with a 3% NaCl solution. The exposure liquid produced in this way will, apart from its NaCl concentration, be close to equilibrium with the pore fluid of the cement paste. These samples are subsequently referred to as "antileach" samples. For the conventionally leached samples the outermost 0.1–1

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mm of the chloride ingress profile may be distorted due to leaching.

To model chloride ingress, the chloride binding properties of the cement pastes have to be known. This is examined in another project [4]. Only a part of the measured chloride profiles will be shown in the text that follows; the full set of measurements can be found elsewhere [3].

2.2. Materials and mixing

The materials used consisted of:

White Portland cement with a Blaine fineness of 420 m^2/kg and the following Bogue calculated phase composition (wt%): C_3S: 66.1, C_2S: 21.2, C_3A: 4.3, C_4AF: 1.1, $C\bar{S}$: 3.5, free CaO: 1.96, Na_2O eq.: 0.17.
Silica fume with a specific surface of 20.5 m^2/g was used: its chemical composition (wt%): SiO_2: 90.8, Fe_2O_3: 0.94, Al_2O_3: 0.54, MgO: 1.32, SO_3: 0.57. The silica fume was added as a dry powder.
Superplasticizer was added at a rate of 1.0% by weight of cement + silica fume at a w/c ratio of 0.2 and 0.3. The superplasticizer was a naphthalene-based dry powder.
Demineralized, freshly boiled water was used (=deaired).

Mixing was performed for 5 min in a 5-L epicyclic laboratory mixer. The water was added in two steps during mixing. This procedure ensures the homogeneity of the paste and the dispersion of the silica fume. The w/c ratio is the weight ratio of water to cement. The silica fume percentage is the weight ratio of silica fume to cement.

2.3. Sample preparation

After mixing, air bubbles were removed from the paste or mortar by evacuation. Thereafter, circular cylindrical moulds with a diameter of approximately 44 mm and a length of 21 mm were filled on a vibrating table. For the first day after mixing the samples were rotated to avoid bleeding. After 1 month of sealed hardening, the samples were demoulded and stored in $Ca(OH)_2$-saturated water for 2 weeks. After this initial water saturation approximately 1 mm was ground off the sample base, which was the chloride-exposed surface. The chloride-exposed surface will thus be an internal surface. The microstructure close to a mould wall or at its air interface is different from the bulk [5]: to eliminate the influence of such a layer, it was removed.

After grinding, a polyurethane coating was applied to all surfaces except the ground base. The polyurethane coating is completely chloride tight and restricted the chloride ingress to be one-dimensional and one-sided.

After application of the polyurethane coating each sample was stored in lime-saturated water under vacuum until the surface dry weight changed less than 0.1% per week. Then the samples were transferred to the chloride exposure jars. The described procedure ensured that the samples were water-saturated to an extent that chloride ingress was not measurably influenced by capillary suction. The total curing time of the samples prior to chloride exposure was approximately 100 days. This ensured a stable cement system in relation to the subsequent chloride exposure time, which in most cases was 1 month.

The water-saturated samples were exposed to a 3% NaCl solution. The chloride and sodium concentrations in the exposure liquids were measured when the exposure was concluded. Within the detection accuracy (approximately 3%) no change in the chloride and sodium concentration of the exposure liquids was observed during the tests.

After removal from the exposure liquid, slices approximately 4-mm thick were cut from the samples. The slices were cut near to the center of the cylindrical samples, parallel to the direction of chloride ingress. Thereafter, the samples were vacuum dried. The slices were cast in epoxy resin and polished to a surface roughness of <1 μm. To avoid alteration to the chloride distribution of the samples, ethanol was used during sample preparation (cutting and polishing). The samples were finally sputter-coated with a conductive carbon layer.

2.4. EPMA measurements

A Cameca SX51 EPMA instrument (Cameca, Courbevoi, France) equipped with four wavelength dispersive spectrometers was used for the chloride profile measurements. An accelerating voltage of 20 kV and a beam current of 20 nA was used. At these conditions the volume of sample analyzed is roughly 1–2 μm^3 for each point.

A mapping technique that included up to 512 × 512 points was used. Chloride ingress profiles were calculated from these maps as an average of all measurements at a certain depth. The EPMA results are given as qualitative measurements based on X-ray "counts" of chlorine, which after correction are proportional to the chloride content [2]. The EPMA measurements presented in the following only show ingressed chloride: The measurements were corrected for background noise and chloride in the raw materials [2]. In order to test the EPMA technique, traditional measurements of chloride profiles were carried out on two samples.

3. Verification of the EPMA measuring technique

Fig. 1 shows chloride profiles measured by EPMA and by the traditional method. As shown the profiles from the two different measuring techniques agree. In addition, the much higher geometric resolution of the EPMA method is demonstrated. This degree of resolution is required for studying high performance cement paste systems.

4. Modelling

A literature review reveals that modelling of chloride ingress in cement paste is a very divisive subject. The cause

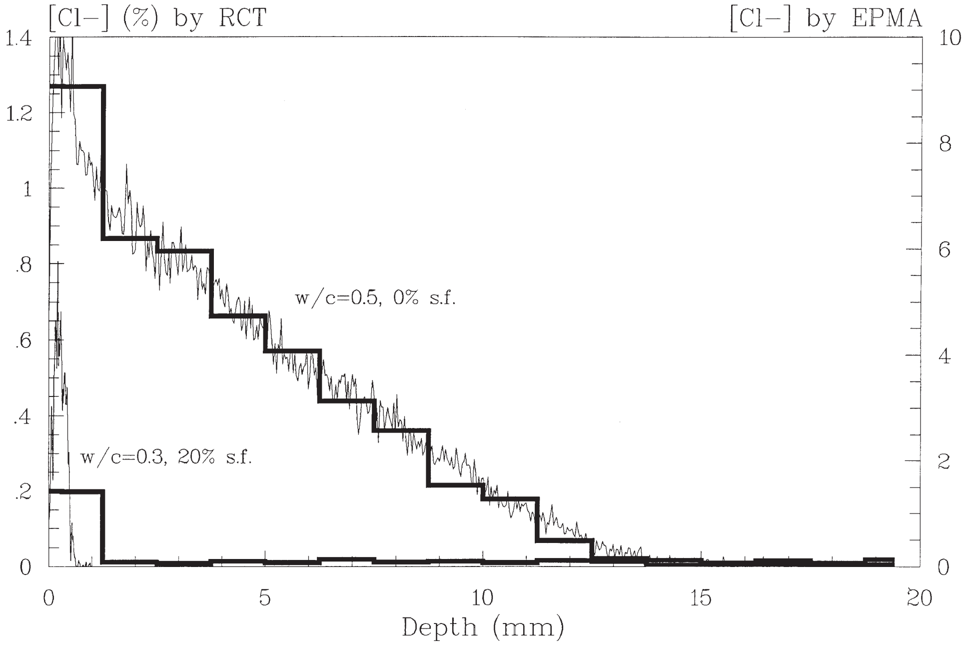


Fig. 1. Comparison of chloride profiles measured by EPMA (thin line) and by the traditional method (broad line). The traditional method is performed with a commercial test kit, Rapid Chloride Test (RCT), (German Instruments, Hellerup, Denmark) where the chloride content is measured in 1.25-mm thick slices cut from the cement pastes. Profiles for two cement pastes are shown: w/c = 0.3 with 20% silica fume addition and w/c = 0.5 without silica fume addition. The pastes were exposed to chloride under leaching conditions for 1 month at 20°C.

seems to be the fact that a number of physical or chemical mechanisms may influence the chloride ingress. At some level, modelling will inevitably neglect some factors; those believed to be less important factors have to be neglected if the model is to be manageable. The aim is to choose the smallest number of characteristics that when combined predict most of the observed behavior. A more complicated theory should not be introduced before it is very sure that it is needed.

The modelling that is performed in this project is based on single component Fick's diffusion modified by binding. The chloride ingress profiles in the cement pastes have been modelled with a computer program based on a first-order finite difference method. Basically, the program contains three elements:

1. Calculation of the cement paste phase composition according to Powers' simplified model [6].
2. Transport of free chloride according to Fick's law: $F = -D\, \partial c_f/\partial x$, where F is the chloride ion flux [kg/(m^{2}s)], c_f is the free chloride concentration (kg/m^3), and x is the ingress depth (m). D is an effective diffusion coefficient (m^2/s) that takes into consideration the tortuosity of the pore system.
3. Chloride binding according to the Freundlich isotherm [7] equation: $c_b = \alpha \cdot c_f^{\beta}$, where c_b (mg/g-gel) is the bound chloride, c_f (mol Cl$^-$/L solution) is the free chloride, and α and β are empirical constants. Note that the unit for c_f in the Freundlich equation is different from the unit for c_f in the diffusion equation. Therefore, unit conversion is done throughout the program.

As seen in Fig. 2, the chloride binding significantly modifies the shape of the chloride ingress profiles, as well as the calculated chloride diffusion coefficients. The strongly concave shape of the Fick profile is qualitatively very different from the measurements; the measured profile is almost linear. If binding is included in the modelling, the description of the measurements is substantially improved. In the case shown, binding leads to an almost linear profile of total chloride content. However, the curvature of the profile depends on the ratio of free to bound chloride. If the w/c ratio is increased, relatively less of the total chloride is bound, and the total profile will be more concave. At equilibrium with a 3% NaCl solution about 75% of the chloride in a cement paste is bound at w/c = 0.2, whereas only about 40% is bound at w/c = 0.7. The shape of the chloride profile at w/c = 0.7 will, therefore, mainly be controlled by the free chloride (i.e., Fick's law). Contrary to this, most of the chloride is present as bound chloride in the cement paste sample at w/c = 0.2. The shape of the chloride profile will in that case be significantly modified by the chloride binding isotherm.

Note that the diffusion coefficient for the pure Fickian profile in Fig. 2 is much lower than the diffusion coefficient when binding is included. The diffusion coefficient, calculated by the pure Fickian profile, lacks physical meaning because binding has to be taken into account artificially by the transport parameter.

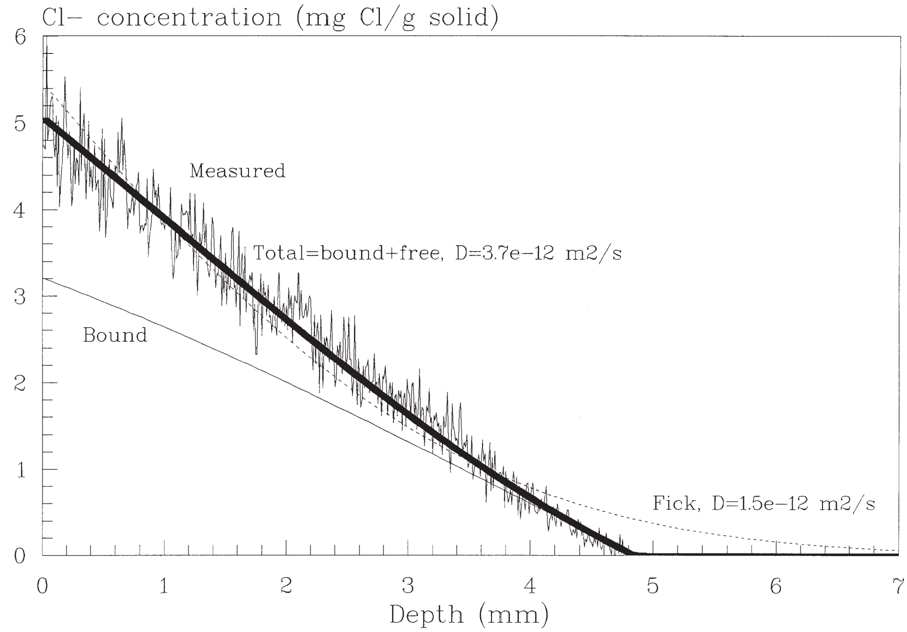


Fig. 2. Example of measured and modelled chloride ingress profile. The paste has w/c = 0.3, 0% silica fume and has been chloride-exposed under antileach conditions for 30 days at 35°C. The fluctuating curve is the measured profile from EPMA mapping. The dashed line is calculated from Fick's law with a diffusion coefficient of $1.5 \cdot 10^{-12}$ m^2/s. The heavy line is calculated assuming that binding occurs. The amount of bound chloride for this profile is shown with the thin line. In this case, the diffusion coefficient for the free chloride is $3.7 \cdot 10^{-12}$ m^2/s.

The Freundlich α and β parameters depend on the silica fume addition and the exposure temperature and have been measured in a chloride binding experiment [4]. As an example, for plain cement paste at 20°C the parameters were determined as $\alpha = 7.0$ mg Cl^-/g gel, and $\beta = 0.4$. However in the chloride ingress modelling it was observed that improved fits were obtained if $\beta = 0.5$ was used. A reason for this may be that the measured β only applies to chloride concentrations in the range approximately 0.01–0.5 mol/L, whereas β increases at lower concentrations [7]. Since the modelling concerns the full concentration range 0–0.5 mol/L, an increased β may take this into account. Another explanation may be that the reduced chloride binding that is implied by the increased β parameter simulates mobility of the bound chloride. In any case, the mentioned modification of the β parameter did not change the estimated diffusion coefficients given later.

As additional data becomes available on chloride binding mechanisms, the semiempirical Freundlich equation could be replaced by more structure-specific factors. For example, the role of Friedel's salt as a chemical binding agent for chloride together with concentration limits for the binding mechanism(s) have recently been presented [8].

There are several additional mechanisms that, in principle, could be taken into account for the chloride ingress model; for example, by including the mobility of bound chloride. However, this has not been done because it is judged that these mechanisms are either too ill-defined or too complicated (or both) to implement in the modelling. At present, there seems to be no reason to include further mechanisms in the model, since the calculated profiles shown later reproduce the measurements reasonably well.

5. Results and discussion

Fig. 3 shows the influence of exposure time on chloride ingress. From the figure it is seen that for a given cement paste the diffusion constant can be assumed to be independent of the exposure time. The systematic change with time, if any, is very small in relation to the other parameters (e.g., silica fume content), which are considered subsequently.

Fig. 4 shows the influence of w/c ratio on chloride ingress. An increased w/c ratio is seen to increase the chloride ingress. A change in the w/c ratio from 0.2 to 0.7 increases the diffusion constant by a factor of almost 50. This is due to the more open and coarse pore structure at the higher w/c ratio. In addition the profile shape seems to depend on the w/c ratio. At w/c = 0.2 the profile is almost linear, whereas it tends to be more concave at higher w/c ratios. This phenomenon is attributed to chloride binding. The lower the w/c, the more chloride will be present as bound chloride relative to free chloride (see the section on modelling).

Fig. 5 shows the influence of silica fume addition on chloride ingress. Silica fume addition reduces the chloride ingress significantly. Addition of 20% silica fume reduces the diffusion constant by a factor of approximately 75. This is attributed to changes in the pore structure such as pore closure and/or a finer pore structure; the intrinsic chloride binding is not significantly changed by silica fume addition [4].

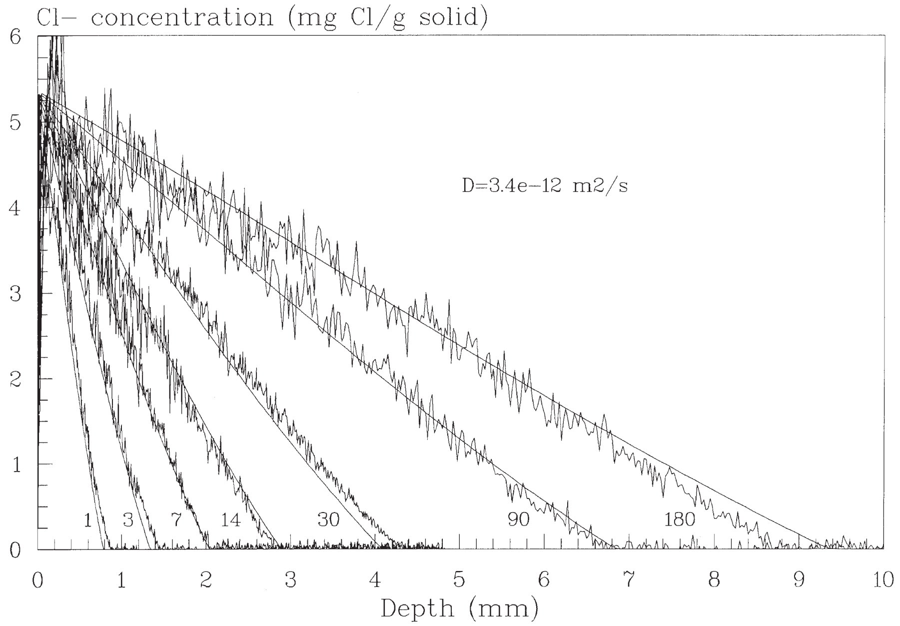
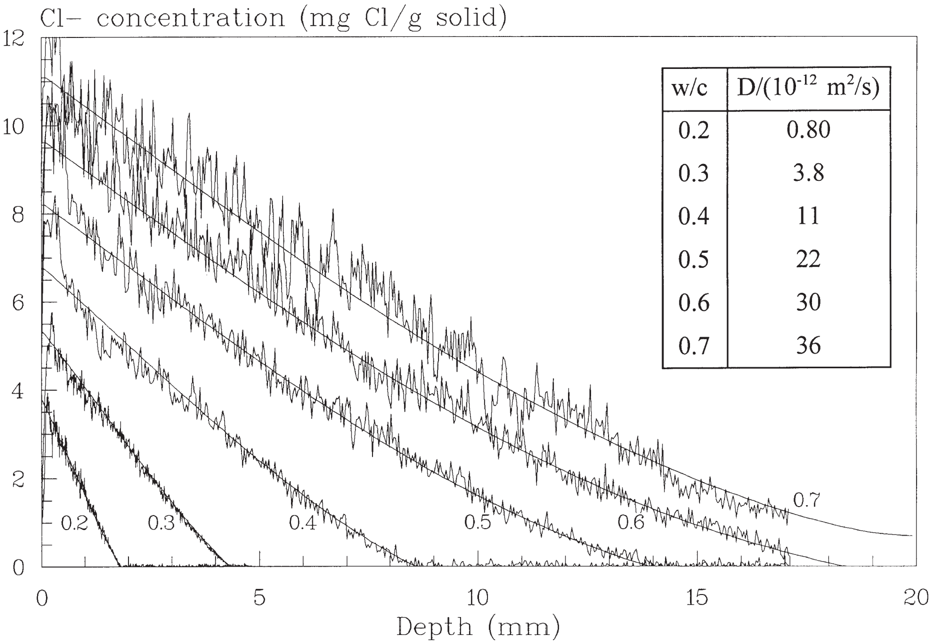


Fig. 3. Influence of exposure time on chloride ingress. Chloride profiles are shown for seven identical cement pastes under leaching conditions with w/c = 0.3 without silica fume addition. The exposure time in days is marked on the curves; the exposure temperature is 20°C. The fluctuating curves are based on EPMA mapping. The smooth curves are calculated profiles with a diffusion coefficient of $D = 3.4 \cdot 10^{-12}$ m^2/s.

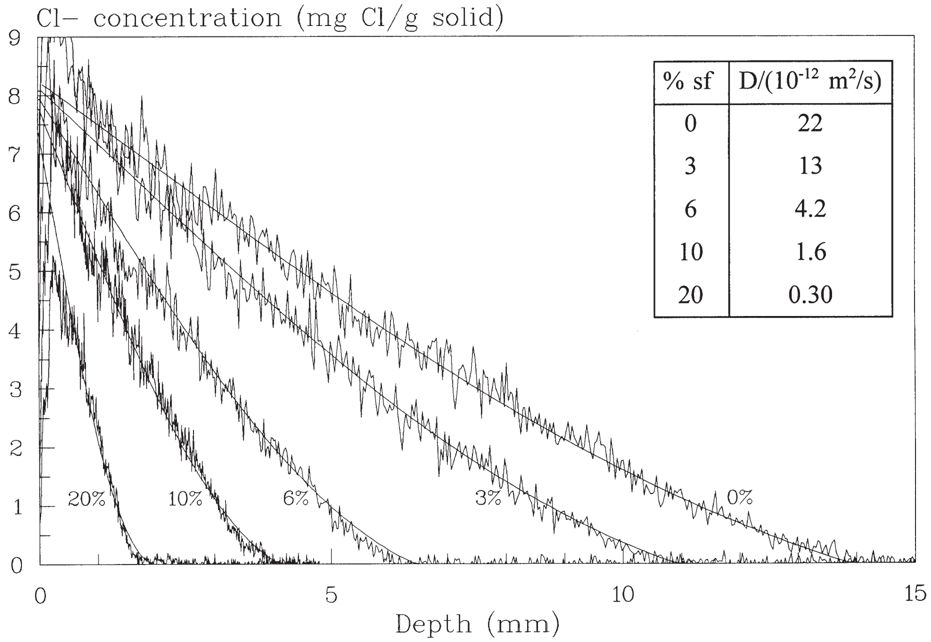
EPMA measurements at different exposure temperatures (not shown) demonstrate that increased temperature accelerates the chloride ingress. This may mainly be due to thermal activation of the diffusion process. However, chloride binding may partly contribute to the observed effect; chloride binding is reduced as the temperature is increased [4].

Based on the EPMA measurements [3] the activation energies for chloride diffusion in two cement pastes have been



w/c	$D/(10^{-12}\ m^2/s)$
0.2	0.80
0.3	3.8
0.4	11
0.5	22
0.6	30
0.7	36

Fig. 4. Influence of w/c ratio on chloride ingress. Chloride profiles for six different pastes are shown. Except for w/c ratio (marked on the curves) the pastes are identical. The pastes do not contain silica fume and have been exposed to chloride under leaching conditions for 1 month at 20°C. The smooth curves are calculated profiles with diffusion coefficients as given in the table. The fluctuating curves are based on EPMA mapping. The full profile at w/c = 0.6 and 0.7 has not been measured by this technique. From line scan measurements it is known that the profile at w/c = 0.6 levels off within the maximum depth of the samples, 20 mm. At w/c = 0.7 the chloride has reached the bottom of the sample and its accumulation alters the tail of the profile.



% sf	$D/(10^{-12}\ m^2/s)$
0	22
3	13
6	4.2
10	1.6
20	0.30

Fig. 5. Influence of silica fume addition on chloride ingress. Chloride profiles in five different pastes are shown. Except for the silica fume addition (marked on the curves) the pastes are identical. The pastes have a w/c ratio of 0.5 and have been exposed to chloride under leaching conditions for 1 month at 20°C. The fluctuating curves are based on EPMA mapping. The smooth curves are calculated profiles; diffusion coefficients are given in the table.

experimentally determined as 33 and 44 kJ/mol. This is in agreement with the range of values reported in the literature (e.g., Page and Lambert [9] give values between 32 and 45 kJ/mol). Note that the activation energy concept of chloride diffusion in cement paste must be considered semiempirical since it is known that chloride diffusion in cement paste is influenced by temperature-dependent factors in addition to pure diffusion [9].

The results shown and discussed so far only refer to pastes. In relation to chloride ingress important micro- and macrostructural differences exist between a cement paste and the corresponding mortar. First of all, the presence of impermeable aggregate particles such as quartz may force the chloride ingress to follow tortuous pathways between the aggregate particles. This will hamper the effective chloride diffusivity. But additionally the mortar does not simply consist of aggregate particles embedded in a homogeneous cement paste matrix. Close to the surface of the aggregate particles the cement paste is more porous compared to bulk cement paste: this is often referred to as the paste-aggregate interfacial transition zone. This may have a thickness of approximately 20 μm and a diffusivity 10 times greater relative to bulk cement paste [10]. Furthermore, in mixtures with a high autogenous shrinkage the restraining effect of the aggregate particles will lead to microcracking of mortars. On the other hand, the corresponding cement paste will remain crack-free if it is unrestrained. Such microcracks may act as chloride ingress routes and hence increase chloride ingress.

From EPMA measurements (not shown) no significant differences in the chloride ingress depth of the mortars relative to the equivalent pastes are observed. These results agree with measurements in the literature [10] where chloride diffusivity was studied in cement pastes and mortars with different sand volume fractions at w/c ratios from 0.25 to 0.45. A further analysis of the results from this study shows that the effective chloride diffusivity within 25% deviation may be considered proportional to the paste volume fraction. This implies that the aggregate has a dilution effect on chloride ingress, but that no major effects from the interfacial transition zone and pathway tortuosity occur. Apparently the observations reported here for cement paste are also valid for mortars.

Fig. 6 shows a plot of the modelled diffusion coefficients for the cement pastes as a function of the capillary porosity. The capillary porosity is calculated with Powers' model based on measured degrees of hydration; for the silica fume systems an extension of Powers' model was used [3,6]. The modelled diffusion coefficients in Fig. 6 are seen to depend strongly on the composition of the cement paste. If the w/c ratio is lowered or silica fume is added to the cement paste the diffusion coefficient diminishes.

The observed strong dependency of the modelled diffusion coefficients on the w/c ratio and the silica fume addition is probably due to differences in the pore structure of the cement pastes. When the porosity is reduced or the tortuosity of the pore system is increased the diffusion coefficient will decrease. Cement paste is a composite material; it is composed of several phases with different properties. The curves in Fig. 6 are based on a composite model that is described in detail elsewhere [3]. In the composite model it is assumed that the cement paste consists of phases that exhibit three types of response:

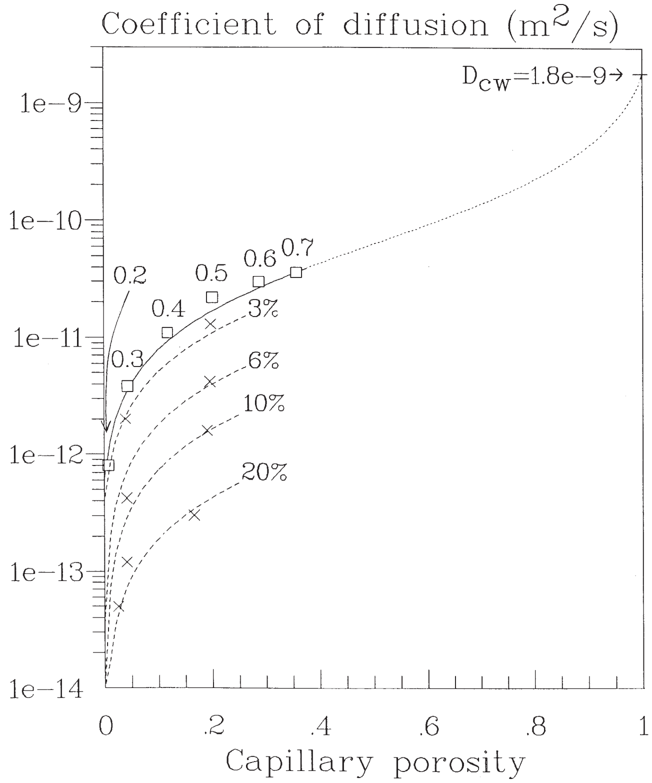


Fig. 6. Diffusion coefficients at 20°C as a function of the capillary porosity. Boxes and crosses are based on the chloride ingress measurements. Boxes represent data on plain cement mixes. An extrapolation of these data to the diffusion coefficient of chloride in free water is suggested by the dotted extension of the trend line. The crosses represent different silica fume additions at w/c ratios 0.3 and 0.5. See text for further explanation.

1. Chloride impermeable calcium hydroxide and unhydrated cement and silica fume.
2. Chloride permeable gel proper (i.e., gel solid and gel water). It is assumed that a bulk diffusivity can be assigned to the gel proper. Together with the calcium hydroxide and unhydrated cement and silica fume the gel proper make up the gel matrix.
3. Chloride permeable capillary water. It is assumed that the chloride diffusion coefficient in the capillary water is identical to that for its self-diffusion in bulk water, $D_{cw} = 1.81 \cdot 10^{-9}$ m/s^2 at 20°C. This value is represented by the curve intersection with a capillary porosity of 1 in Fig. 6.

According to the composite modelling the diffusivity of chloride in the gel matrix varies only slightly as a function of the w/c ratio. That implies that the diffusivity of plain cement paste is mainly determined by the capillary porosity. This is in agreement with Garboczi and Bentz [11].

Silica fume added to the cement pastes significantly lowers the measured diffusion coefficients (see Fig. 6). This may partly be due to a reduced connectivity of the capillary pore system. However, according to the applied composite theoretical model, the silica fume addition also reduces the bulk diffusivity of chloride in the gel proper; it is reduced by a factor of 1000 by addition of 20% silica fume. Garboczi and Bentz [11] have previously speculated whether silica fume addition reduces the diffusivity for ions in the C-S-H gel phase.

6. Conclusion

This paper deals with chloride ingress in cement paste and mortar measured with EPMA. Approximately 50 different cement paste and mortar samples have been examined, ranging from traditional to modern high-performance types. The pastes and mortars were exposed to synthetic seawater from 1 day to half a year.

The measured results have been modelled with a computer program that simulates chloride ingress in cement paste. The program assumes that chloride is transported by monocomponent diffusion according to Fick’s law, that chloride is bound by the cement gel according to a Freundlich isotherm, and that Powers’ simplified model describes the phase distribution of a cement paste. The simulated ingress profiles closely resemble the measurements. Presently there seems to be no need to include further mechanisms in the model.

The experiments show that both the composition of the paste and mortar as well as the exposure conditions have a strong influence on the chloride ingress. Of the more important observations it can be noted that quartz aggregate addition to cement paste can be considered to have a pure dilution effect from a chloride ingress point of view. Comparison of mortar and cement paste ingress profiles also indicate that internal microcracking due to autogenous shrinkage has no overall effect on the chloride ingress.

From measurements with various exposure times it seems that the diffusion coefficient can be considered a constant for a given cement paste; it does not depend on exposure time or ingress depth. The influence of the temperature on the diffusion coefficient for two cement pastes has been described with activation energies of 33 and 44 kJ/mol, respectively.

The influence of w/c ratio and silica fume addition has been simulated with a composite theoretical model. According to the composite model the measured change in diffusion coefficient as a function of the w/c ratio can be related solely to the capillary porosity of the pastes. Contrary to this, the observed strong reduction of the diffusion coefficient when silica fume is added may be due to a change of the gel proper or a reduced connectivity of the capillary pore system.

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