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Prediction of Chloride Ingress and Binding in Concrete

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Abstract

This paper summarizes recent work on an analytical model for predicting the ingress rate of chlorides in cement-based materials. A thermodynamic model for the phase equilibria in hydrated Portland cement based on the application of the phase rule was developed. The model's applicability to predict chloride binding in Portland cement pastes at any content of chloride, alkalis, sulfates and carbonate was verified experimentally and found to be consistent with data in the literature. The thermodynamic model for the phase equilibria in hydrated Portland cement was introduced into an existing Finite Difference Model for the ingress of chlorides into concrete accounting for its multi-component nature, and the composite theory was used for predicting the diffusivity of each ion based on the phases present, i.e. the phase assemblage, in the hydrated Portland cement paste. Agreement was found between chloride/calcium profiles predicted by the model and those determined experimentally on 0.45 water-to-powder Portland cement pastes exposed to 650 mM NaCl for 70 days. Measured chloride ingress was found to be a factor of five higher than predicted by the model. The effective diffusion rate of sodium and potassium was found more than 100 times lower than the effective diffusion rate of chloride.

1. Introduction

Service life prediction is becoming an inherent tool for design and redesign of reinforced concrete structures. For structures in marine environment and structures exposed to de-icing salt the risk of chloride induced reinforcement corrosion must be considered. For design purposes the service life of such structures is often divided into an initiation phase, i.e. the time to onset of corrosion, and a propagation phase [Tuutti 1982].

Corrosion rates for chloride-induced corrosion are generally high and the mechanisms and resulting effects are difficult to model. Therefore, service life is often modeled as the duration of the initiation period plus experienced based duration of the propagation period, e.g. in [Johnsen et al. 2003]. Modeling of the initiation period requires knowledge of the chloride ingress rate and the critical chloride concentration for initiation of reinforcement corrosion.

Predictive models, such as the DuraCrete model [Engelund et al 2000], Life-365 [Bentz and Thomas 2001], and the HETEK model [Nilsson et al. 1997], all make use of a combination of ingress models and experimentally based material parameters. Recently, it has been shown that the critical chloride concentration for initiation of reinforcement corrosion is strongly dependent on the amounts of interfacial defects [Buenfeld et al 2003], [Nygaard 2003]. However, this topic will not be dealt with in this paper.

The aim of a recent study [Nielsen 2004] was to provide an analytical model for predicting the ingress rate of chlorides in cement-based materials. A thermodynamic model for the phase equilibria in hydrated Portland cement based on the application of the phase rule was developed [Nielsen et al. 2005a]. This approach was extended to include the reactions resulting in the binding of chlorides and alkalis [Nielsen et al. 2005b]. The model's accuracy to predict chloride binding in Portland cement pastes at any content of chloride, alkalis, sulfates and carbonate was verified experimentally and found to be consistent with data in the literature [Nielsen et al. 2004]. Furthermore, the model was shown to be equally valid for the phases present, i.e. the phase assemblage identified in 25 years old Portland cement pastes exposed to sodium chloride [Nielsen 2004].

The thermodynamic model for the phase equilibria in hydrated Portland cement was introduced into an existing Finite Difference Model (FDM) for the ingress of chlorides into concrete. This model accounts for the multi-component nature of the pore solution. The composite theory was used for predicting the diffusivity of each ion based on the phase assemblage in the hydrated Portland cement paste. Agreement was found between chloride/calcium profiles predicted by the model and those determined experimentally on 0.45 water-to-powder (w/p) Portland cement pastes exposed to 650 mM NaCl for 70 days. Measured chloride ingress was found to be a factor of five higher than predicted by the model. The effective diffusion rate of sodium and potassium was found more than 100 times lower than the effective diffusion rate of chloride.

The present paper summarizes the modeling approach. For detailed information reference is given to the PhD thesis by Nielsen [2004] and work published in journals and conference proceedings by Nielsen et al. referred to in the text.

2. Estimation of phase assemblage in hydrated Portland cement without chloride and alkalies

Portland cement clinker mainly consists of the clinker phases C_3S[1] ($3CaO.SiO_2$) and C_2S ($2CaO.SiO_2$) and, to varying extents, C_3A ($3CaO.Al_2O_3$) and C_4AF ($4CaO.Al_2O_3.Fe_2O_3$). Upon grinding of the clinkers, $CaSO_4$ is added to regulate setting of the finished cement. The $CaSO_4$ may be present as a mixture of gypsum, hemihydrate and anhydrite. Portland cement is unstable in the presence of water, resulting in a solid matrix of reaction products after hydration.

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[1] Cement chemistry notation is used

The relative content and composition of phases present in hydrated Portland cement can be calculated from the chemical composition of the cement and the water/cement ratio. How this can be undertaken is described in this section, which for simplicity starts out with a simple system, CaO-SiO_2-H_2O. Progressively, components are added until the complex cement paste system with all significant components is achieved. As the thermodynamic approach is not traditionally applied in civil engineering a short background for the estimation of phase assemblage in hydrated Portland cement is also given.

The number of independent variables describing the state of a system in equilibrium (degrees of freedom, F) is given by the 'phase rule' of J. Willard Gibbs. For non-reacting systems the phase rule is; $P + F = C+2$, where P is the number of phases and C is the number of chemical species or components [Putnis and McConnell 1980]. The phase rule for systems at constant temperature and pressure is reduced to; $P+F = C$. If the composition of all phases in the system are fixed and independent, the relationship becomes; $P = C$. A system obeying this relationship is said to be invariant.

Equilibrium is a static condition in which no changes occur in the macroscopic properties of a system with time. However, in engineering practice, the assumption of equilibrium is normally justified when it leads to results of satisfactory accuracy [Putnis and McConnell 1980].

2.1 CaO-SiO_2-H_2O

The phase diagram for the three-component system CaO-SiO_2-H_2O is given in Figure 1. CaO and SiO_2 results from the dissolution of the clinker phases C_2S and C_3S (only C_3S is shown in figure 1) and, depending on the overall concentration of each species in solution, precipitate according to the diagram.

A fully hydrated paste of C_3S and C_2S in ratios as found in Portland cement paste is composed of a poorly crystalline calcium silicate hydrate phase ($C_{1.75}SH_4$), calcium hydroxide (CH) and the pore solution, corresponding to the lower lightly shaded region in Figure 1. As three phases are present in this region, the system is invariant according to the 'phase rule' (F=0). Thus, as long as the overall composition of the system lies within the region the composition of each of these phases must be constant. The Ca/Si ratio of the C-S-H at 1.75 is in good agreement with observations in [Taylor 1997], [Richardson 2000], and [Famy et al. 2002].

If the relative content of SiO_2 increases significantly, which would be the case of Portland cement pastes with large contents of silica fume, CH may become exhausted, resulting in the presence of only two phases in the subsystem; a C-S-H phase with Ca/Si molar ratio between 0.80 and 1.75 and the pore solution.

2.2 CaO-Al_2O_3-SO_3-(Fe_2O_3)-(CO_2)-SiO_2-H_2O

In this section further components (Al_2O_3, SO_3, Fe_2O_3, CO_2) are added to the CaO-SiO_2-H_2O system to resample the complex cement paste system. The main source of Al_2O_3 is the clinker mineral C_3A, and the source of SO_3 is the added $CaSO_4$ (gypsum, hemihydrate or anhydrite) during grinding of the clinkers. These minerals, as well as C_3S and C_2S, react relatively fast

[Taylor 1997], which is why after a few months of hydration the phase assemblage of the hydrated part of the cement can be assumed to be metastable.
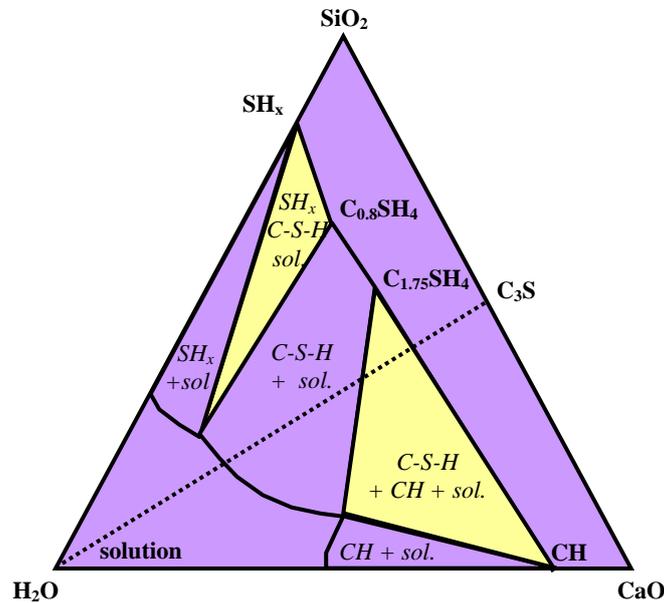

Figure 1   Phase diagram for the three-component system CaO-SiO_2-H_2O. Adapted from [Taylor 1997] in [Nielsen 2004]

The contents of Al_2O_3 and SO_3 in Portland cements are low compared to CaO and SiO_2. Thus, even a substantial amount of CaO combines with Al_2O_3 and SO_3, the phase relationships in Figure 1 remain essentially the same. Some of the Al_2O_3 and SO_3 are incorporated in the C-S-H phase. Based on single point EDS[2] the following ratios were identified; S/Ca = 0.03 and Al/Ca = 0.04 [Nielsen et al. 2005a]. These values are in accordance with findings by Famy et al. [2002]. Thus, in hydrated Portland cement pastes the presence of Al_2O_3 and SO_3 would only result in a change in the relative amount of CH to C-S-H and the composition of C-S-H.

At ages less than one year or so the composition of the hydroxy-AFm[3] phase is most likely to be C_4AH_{13} (e.g. [Taylor 1997]) or C_4AH_{18} (e.g. [Kuzel and Pöllmann 1991]), but in older pastes the more stable phase hydrogarnet, C_3AH_6, is likely to occur instead [Taylor 1997], [Damidot and Glasser 1995].

Iron oxide (Fe_2O_3) is likely to form a goethite-like hydrate; FH_3 [Taylor and Newbury 1984]. Furthermore, Fe_2O_3 appears to be incorporated to some extent in the C-S-H structure

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[2] EDS: Energy dispersion Spectroscopy at 15 keV, 25 µA and 40 s per point

[3] AFm is aluminum ferrite compounds with a single (mono) formula unit CaX_2.

corresponding to a Fe/Ca molar ratio of approx. 0.02. [Nielsen et al. 2005a], [Nielsen et al. 2005b]

Regarding the effect of carbonate (here represented by CO_2), Damidot and Glasser [1995] concluded for the system $CaO-Al_2O_3-SO_3-Fe_2O_3-CO_2-SiO_2-H_2O$ that hemicarbonate ($C_3A.\frac{1}{2}CaCO_3.\frac{1}{2}Ca(OH)_2.11\frac{1}{2}H_2O$) is only stable at low concentrations of carbonate and sulfate and high concentrations of calcium while monocarbonate ($C_3A.CaCO_3.11H_2O$) is stable over a wider range of concentrations. They further suggested that monocarbonate preferentially forms in systems were alkalis are present.

2.3 Model for the phase equilibria in hydrated Portland cement

Portland cement paste typically has seven major components (i.e. SiO_2, Al_2O_3, CaO, Fe_2O_3, SO_3, CO_2, H_2O). The phase assemblages described above are therefore relevant. Furthermore, from the aqueous phase diagram in Figure 2 it is observed that CH is stable in hydrated Portland cements with the assemblages described.

According to the phase rule, a maximum of seven phases (six hydrate phases and the pore solution) can be formed at constant temperature and pressure. Based on the above four assemblages are possible, see Table 1.

In a fully hydrated Portland cement, which as a first approximation is invariant at constant temperature and pressure, the relative contents of phases of known composition present can be calculated by solving 'n' equations for 'n' unknowns, where 'n' is the number of both components and phases. Since the system is invariant, the composition of each of the phases remains constant. Relevant physical properties of the phases described earlier can be found in the literature, e.g. [Taylor 1997] and [Lea 1970]. Values for the density and amount of evaporable water in C-S-H are proposed in [Nielsen et al. 2005a].

Table 1 Possible phase assemblages in Portland cement paste[4].

1.	C_4AH_{13}, monosulfate, monocarbonate, …	
2.	monosulfate, ettringite, monocarbonate, …	$C_{1.75}SH_4$, FH_3, CH, Pore solution
3.	Ettringite, monocarbonate, calcite, ...	
4.	Ettringite, calcite, gypsum, ...	

3. Estimation of phase assemblage in hydrated Portland cement with chloride and alkalies

This section summarizes the phase diagrams applicable for hydrated Portland cement paste exposed to chloride, sulfate and carbonate as well as findings on the pore solution composition.

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[4] Phases not already mentioned in the text: Monosulphate: $C_3A.CaSO_4.12H_2O$ Ettringite: $C_3A.3CaSO_4.32H_2O$, Calcite: $CaCO_3$

On this basis a model, for estimation of phase assemblage in hydrated Portland cement with chloride and alkalies, is provided.
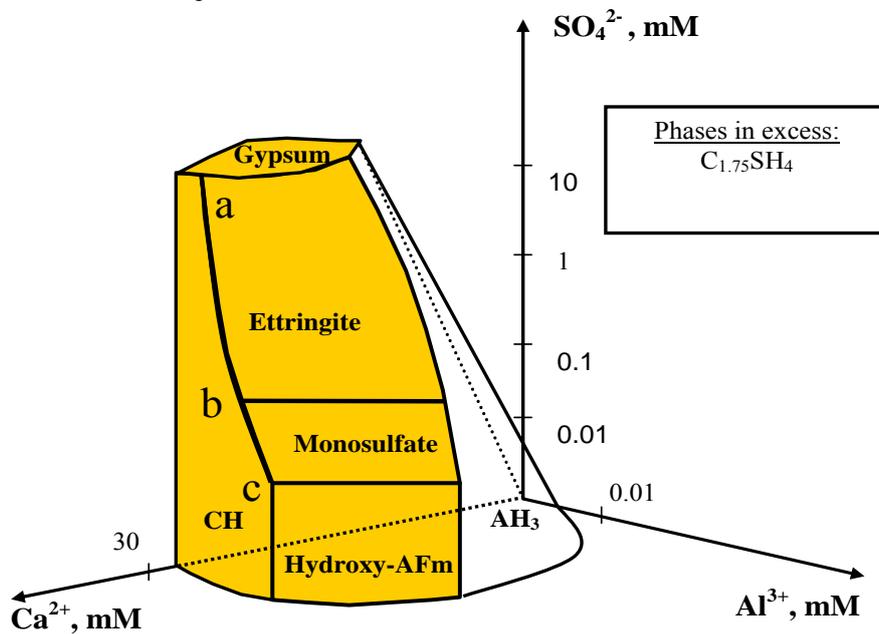

Figure 2   Aqueous phase diagram for the system $CaO\text{-}Al_2O_3\text{-}SO_3\text{-}SiO_2\text{-}H_2O$, for the case where $C_{1.75}SH_4$ is stable. Adapted from [Damidot and Glasser 1993]. Invariant points a, b and c do not necessarily correspond to the scale given on the axes. [Nielsen 2004]

Figures 3 to 6 illustrate phase diagrams for relevant subsystems of the system $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3\text{-}SO_3\text{-}CaCl_2\text{-}CO_2\text{-}Na_2O\text{-}H_2O$, which are the main components in hydrated Portland cement. The subsystem $CaO\text{-}SiO_2\text{-}H_2O$ is the same as that presented in figure 1. The composition of the pore solution as well as content of alkalis in the C-S-H can be calculated from the relationships given in Table 2.

The system $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3\text{-}SO_3\text{-}CaCl_2\text{-}CO_2\text{-}H_2O$ (no alkalies) is thoroughly described in [Nielsen et al. 2003]. A solid solution between Friedel's salt and monocarbonate "AFmss"[5] was found, which introduce a degree of freedom to the system, see Figure 3. This permits the relative content of Friedel's salt to increase in the AFmss along with a simultaneous increase in the concentration of chloride ions in both the pore solution and in the C-S-H phase. The phase rule is satisfied as long as a single relationship exists for the distribution of chloride between all three phases. The distribution function for chloride between the C-S-H and the solid solution phase is independent of the alkali content, but is dependent on the iron content of the system.

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[5] "ss" denotes solid solution

Sodium and potassium are considered to have the same properties and to show similar behavior, which is supported by the observation by Hong and Glasser [1999 and 2002]. The presence of sodium in a chloride containing cement paste system has to be defined by at least two additional components. In the solid phases it can be described by the element NaOH (which can be expressed by the relative contents of the components Na_2O and H_2O), whilst the components Na_2O, NaCl and H_2O must be defined in the pore solution in order to express the presence of NaCl and NaOH [Nielsen et al 2005b]. At low concentrations of chloride, the composition of the pore solution can be expressed by relative contents of NaCl, Na_2O, and H_2O. Once all sodium is balanced by chlorides, any further addition of chlorides can be expressed by the increase in $CaCl_2$ concentration, where Ca^{2+} is released from the solid phases [Nielsen et al 2005b].

The overall reaction, which takes place in hydrated Portland cement pastes exposed to chloride accounting for the total content of alkalis and the relative amount of solution to solid paste, is given in Table 2 (see [Nielsen et al 2005b] for details). The overall reaction is divided into two parts; one for the C-S-H which contains alkalis, the other for the alkali-free C-S-H. The overall reaction not only describes the distribution of chlorides between the C-S-H, AFmss, and pore solution, but also for the change in Ca^{2+}, OH^-, and alkali concentrations in the pore solution.
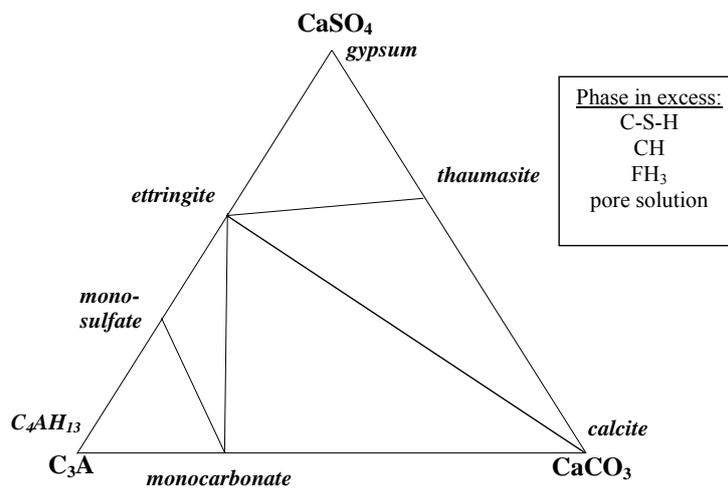

Figure 3   Subsystem C_3A-$CaSO_4$-$CaCO_3$ of the system SiO_2-Al_2O_3-SO_3-Fe_2O_3-CaO-Na_2O-CO_2-$CaCl_2$-$NaCl$-H_2O for hydrated Portland cement. C_3A does not refer to the normative content C_3A in the clinker, but to the total Al_2O_3. From [Nielsen 2004].[6]

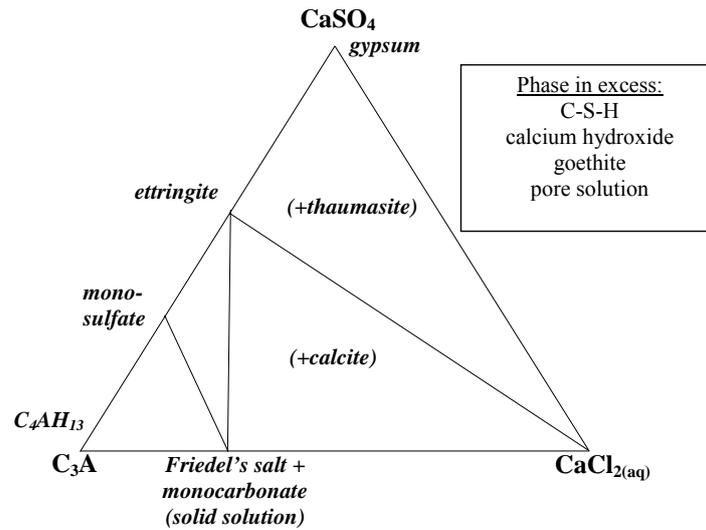[6] Phases not already mentioned in the text: Thaumasite: $[Ca_3Si(OH)_6.12H_2O](SO_4)(CO_3)$

Figure 4   Subsystem C_3A-$CaSO_4$-$CaCO_3$ of the system SiO_2-Al_2O_3-SO_3-Fe_2O_3-CaO-Na_2O-CO_2-$CaCl_2$-$NaCl$-H_2O for hydrated Portland cement. C_3A does not refer to the normative content C_3A in the clinker, but to the total Al_2O_3. From [Nielsen 2004].

Figure 5   Subsystem C_3A-$CaCl_2$-$CaCO_3$ of the system SiO_2-Al_2O_3-SO_3-Fe_2O_3-CaO-Na_2O-CO_2-$CaCl_2$-$NaCl$-H_2O for hydrated Portland cement. C_3A does not refer to the normative content C_3A in the clinker, but to the total Al_2O_3. From [Nielsen 2004].[7]
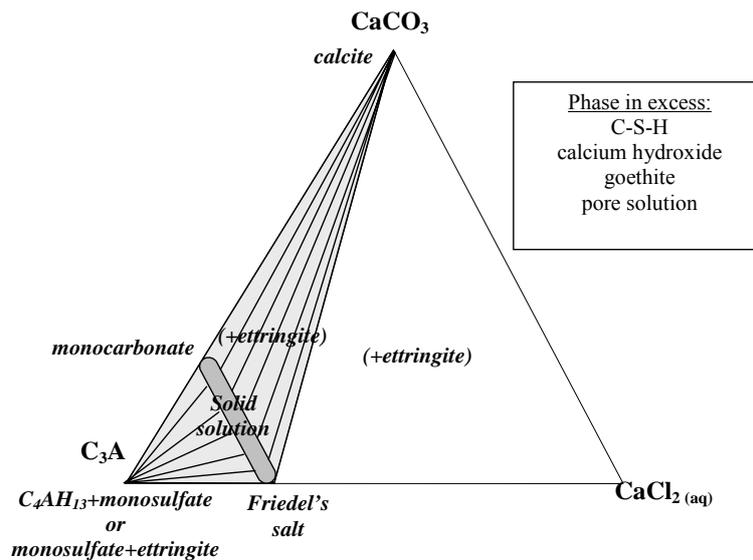

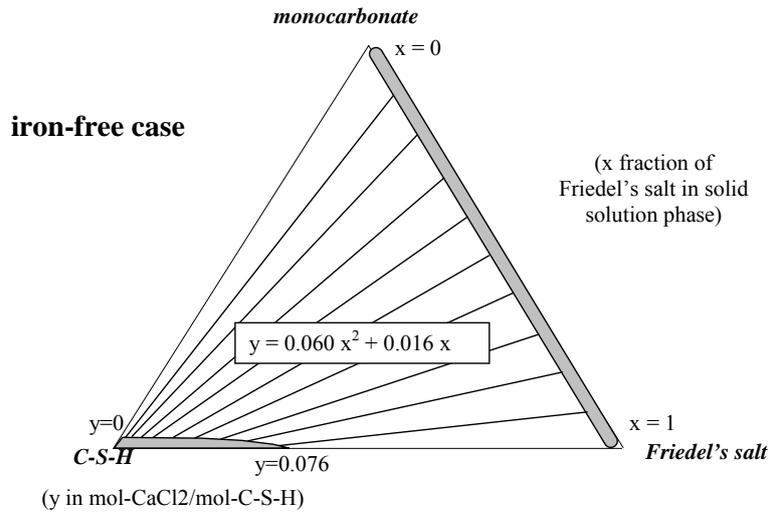[7] Phases not already mentioned in the text: Friedel's salt: $C_3A.CaCl_2.10H_2O$

Figure 6   Pseudo ternary subsystem for "C-S-H – monocarbonate- Friedel's salt" in the SiO_2-Al_2O_3-SO_3-Fe_2O_3-CaO-Na_2O-CO_2-$CaCl_2$-$NaCl$-H_2O system for hydrated Portland cement (notice: iron-free case; i.e. white Portland cement). C-S-H corner is not-to-scale. From [Nielsen 2004].

4. Prediction of ingress rate

Based on a computation model for the diffusion of multi-species in solution [Truc 2000] a FDM for simulating the ingress of chlorides in cement-based materials was developed [Nielsen 2004]. This FDM model takes into account a) the phase assemblage present and b) the effect of capillary porosity of the hydrated paste on the effective diffusion coefficient. The FDM is based on the assumption of instantaneous binding reactions.

The model for phase assemblage was presented above, whereas the estimation of diffusion coefficients is described below. The effective diffusion coefficients for each species in solution during transport through a hydrated Portland cement paste can be estimated by application of the composite theory [Jensen 1999]. The procedure is e.g. described in [Nielsen and Geiker 2003], where the water-filled porosity was estimated by means of Powers' model and sorption isotherms. However, Powers' model does not take into account the difference in density of the various phases formed.

Table 2 Overall reaction describing the binding of chloride by the C-S-H and AFm phases, and the composition of the pore solution. From [Nielsen 2004]

1.a) Chloride binding in PC pastes in which Na is still present in the C-S-H, and no AFm phases other than monocarbonate are present.

$$\mathbf{b} \cdot [C_3A.CaCO_3.11H_2O]_{(s)} + \mathbf{a} \cdot [1.75CaO.SiO_2.\mathbf{z}NaOH.4H_2O]_{(s)} +$$
$$+ ((\mathbf{k+1}) \cdot \mathbf{y \cdot a} + \mathbf{b \cdot x}) \, CaCl_{2\,(aq)} + \mathbf{2 \cdot 0.83 \cdot k \cdot y \cdot a} \, NaOH_{(aq)}$$
$$\downarrow$$
$$\mathbf{2 \cdot k \cdot y \cdot a} \, NaCl_{(aq)} + \mathbf{a} \, [1.75CaO.SiO_2.(\mathbf{z \text{-} 0.34 \cdot k \cdot y})NaOH.yCaCl_2.4H_2O]_{(s)}$$
$$+ \mathbf{k \cdot y \cdot a} \, Ca(OH)_{2\,(s)} + \mathbf{b} \, [C_3A.CaCl_{2\,(\mathbf{x})}.CaCO_{3\,(\mathbf{1\text{-}x})}.11H_2O]_{(s)} + \mathbf{b \cdot x} \, CaCO_{3\,(s)}$$

1.b) Chloride binding in PC pastes in which Na is still present in the C-S-H, and other AFm phases than monocarbonate are present

$$\mathbf{b} \cdot [C_3A.CaCO_3.11H_2O]_{(s)} + \mathbf{a} \cdot [1.75CaO.SiO_2.\mathbf{z}NaOH.4H_2O]_{(s)} +$$
$$+ ((\mathbf{k+1}) \cdot \mathbf{y \cdot a} + \mathbf{b \cdot x}) \, CaCl_{2\,(aq)} + \mathbf{2 \cdot 0.83 \cdot k \cdot y \cdot a} \, NaOH_{(aq)}$$
$$\downarrow$$
$$\mathbf{2 \cdot k \cdot y \cdot a} \, NaCl_{(aq)} + \mathbf{a} \, [1.75CaO.SiO_2.(\mathbf{z \text{-} 0.34 \cdot k \cdot y})NaOH.yCaCl_2.4H_2O]_{(s)}$$
$$+ \mathbf{k \cdot y \cdot a} \, Ca(OH)_{2\,(s)} + (\mathbf{b+bx}) \, [C_3A.CaCl_{2\,(\mathbf{x})}.CaCO_{3\,(\mathbf{1\text{-}x})}.11H_2O]_{(s)}$$

2. Chloride binding in Portland cement pastes with alkali-free C-S-H

$$\mathbf{b} \cdot [C_3A.CaCl_{2\,(\mathbf{m})}.CaCO_{3\,(\mathbf{1\text{-}m})}.11H_2O]_{(s)} + (\mathbf{b \cdot x} + \mathbf{y \cdot a}) \, CaCl_{2\,(aq)} +$$
$$+ \mathbf{a} \, [1.75CaO.SiO_2.(\mathbf{z/0.34 \cdot k})CaCl_2.4H_2O]_{(s)}$$
$$\downarrow$$
$$\mathbf{a} \cdot [\, (\mathbf{1.75\text{-}y})CaO.SiO_2.(\mathbf{z/(0.34 \cdot k)} + \mathbf{y})CaCl_2.(\mathbf{4 - y})H_2O]_{(s)} + \mathbf{y \cdot a} \, Ca(OH)_{2\,(s)} +$$
$$+ \mathbf{b} \cdot [C_3A.CaCl_{2\,(\mathbf{m + x})}.CaCO_{3\,(\mathbf{1\text{-}m\text{-}x})}.11H_2O]_{(s)} + \mathbf{b \cdot x} \, CaCO_{3\,(s)}$$

Note: in eq.2, for each mol of $CaCl_2$ bound by the C-S-H, $(\mathbf{PS/a})/75$ mol $CaCl_2$ remain in solution, where PS denotes the amount of solution in millilitre (i.e. pore solution + exposure solution, if applicable).

- '$\mathbf{x}$' denotes the fraction of Friedel's salt in the AFm solid solution phase; '$\mathbf{y}$' denotes the content of $CaCl_2$ in the C-S-H, in mol/mol, and is related to '$\mathbf{x}$' as follows,

In the iron-free case (white Portland cement)

$$\mathbf{y} = 0.0601 \, \mathbf{x}^2 + 0.0164 \, \mathbf{x}$$

In the iron-containing case (grey Portland cement)

$$\mathbf{y} = 0.0376 \, \mathbf{x}^2 + 0.0046 \, \mathbf{x}$$

- '$\mathbf{a}$' is the content of C-S-H, in mol; '$\mathbf{b}$' is the initial content of monocarbonate, in mol.

- '$\mathbf{z}$' is the molar ratio of NaOH, in the chloride-free C-S-H, to C-S-H, i.e. in mol/mol. This can be calculated from the initial Rd, i.e. 0.65 (see the text), which is a general value, independent of water to powder ratio.

- '$\mathbf{k}$' is defined as

$$\mathbf{k} = \mathbf{z} \cdot (\mathbf{PS/a}) \cdot 25 / (0.83 \cdot 0.81 \cdot M_{w,\text{C-S-H}} \cdot Rd_0) = \mathbf{z} \cdot (\mathbf{PS/a}) \cdot 0.2354$$, where $\mathbf{PS}$ is the amount of solution in milliliter (i.e. pore solution + exposure solution, if applicable).

- '$\mathbf{m}$' denotes the fraction of Friedel's salt in the solid solution phase at the chloride content where all alkalis have been released to the pore solution from the C-S-H.

4.1 Estimation of effective diffusion coefficients

Based on an equation from Maxwell for the diffusion coefficient of a composite Jensen [1999] proposed an equation for the diffusion coefficient of the gel matrix, D_{gm}. The gel matrix was defined as the total volume of solid gel products, gel water, and unhydrated cement particles. According to the model described in section 2 the gel matrix corresponds to the volume fraction occupied by all phases in the hydrated Portland cement paste, excluding only the capillary porosity. Jensen [1999] assumed that CH and unhydrated cement particles are impenetrable by ions. Nielsen [2004] further assumed that also calcite, gypsum, goethite, and brucite are impenetrable for ions, i.e.;

$$D_{gm,i} = D_{gp,i} \frac{V_{gp}}{V_{gp} + \frac{3}{2}(V_{ce} + V_{CH} + V_{calcite} + V_{gypsum} + V_{goethite} + V_{brucite})}$$

where D_{gp} is the diffusion coefficient of the so-called gel proper (gel solid and gel water). Garboczi has proposed a diffusion coefficient of chloride ions in the gel proper corresponding to 1/400 of the diffusion coefficient through water-filled capillaries, D_{cw}. It is assumed as a first approximation that the same applies for all other species. Assuming phase symmetric crumbled foil composites, Fuglsang-Nielsen [2004] proposed the following equation for the diffusion coefficient through the cement paste, D_p,

$$D_{p,i} = D_{gm,i} \frac{n + 2\sqrt{n} \cdot (1 + c \cdot (n-1))}{n + 2\sqrt{n} - c \cdot (n-1)}$$

where n is defined by the ratio of D_{cw} to D_{gm}, i.e. 1/400, and c is the total volume fraction of capillary porosity. Finally, if the aggregates are impermeable, the effective diffusion coefficient, D_{eff}, through a mortar or concrete can be predicted by the following equation proposed by Maxwell [mentioned e.g. in Jensen [1999],

$$D_{eff,i} = D_{p,i} \frac{1}{1 + \varphi/2}(1 - \varphi)$$

where φ is the volume fraction of aggregates and air.

The effect of degree of saturation can be taking into account by assuming only part of the capillary pores to be water filled, see [Nielsen and Geiker 2003].

4.2 Testing of the ingress model

To test the applicability of the ingress model the ingress of NaCl in hydrated Portland cement pastes (w/p 0.45) was studied at a maturity of 4.5 months [Nielsen 2004]. Here, results of ingress in a white Portland cement with 12 % C_3A are presented.

The samples were exposed to unidirectional ingress of a 650 mM NaCl solution for 70 days. The volume of exposure solution to volume of samples was high (approx. 36). Therefore, the pH of the exposure solution never exceeded 9.5 and the concentration of NaCl remained

constant within ± 20 mmol/l. Analyses of the composition as a function of depth were carried out by EDS. Perpendicular to the exposed surface three line-scans with spacing of approx. 4 mm were undertaken at step increments of 50 μm until a depth of 15 mm[8]; these measurements are referred to as profiles in the following. Furthermore, parallel to the surface at depths of 2, 4, 6, 10 and 15 mm line-scans of 200 randomly located points were performed. The latter measurements were used to investigate the phase assemblage as a function of depth.

Measured vs. predicted molar ratios of Cl to Ca in the solid solution phase of monocarbonate and Friedel's salt (AFmss) at the depths of 2, 4, 6, 10 and 15 mm were compared, see Figure 7. The good agreement between predicted and measured Cl to Ca ratios supports the assumption of quasi-instantaneous binding.
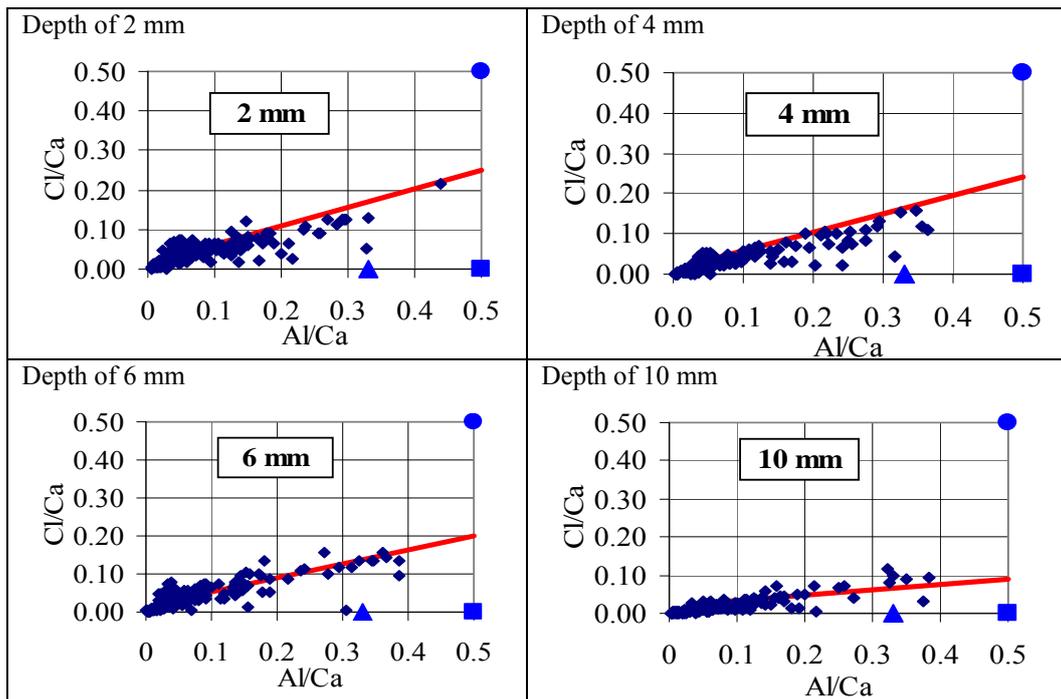

Figure 7: Measured vs. predicted molar ratio of Cl to Ca in the solid solution phase at different depths fro the surface exposed to unidirectional ingress of 650 mM NaCl for 70 days at 20°C (w/p 0.45 WPC(12) paste with 1 wt. % replacement of powder by calcite. After [Nielsen 2004]. ▲Ettringite, ■Monocarbonate, ●Friedel's Salt

The ingress of sodium in the Portland cement pastes was much slower than the ingress of chloride. This does not agree with the multi-species theory, where chloride and sodium are expected to have similar ingress rates, if no reaction with the concrete took place, resulting

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[8] Reduced measuring time at each point from 40 s to 14 s

from the electrical field between the ions in solution. The leaching of potassium was also observed to be much slower than expected. The observations are in accordance with that reported in [Volkwein 1995]. A possible explanation could be that the model is based on the assumption of instantaneous binding reactions. Hydroxyl could be more readily available from dissolution of CH than absorption and desorption of alkalis in the C-S-H, resulting in a faster ingress of chloride compared to that of sodium due to fast leaching of hydroxyl.

The measured molar ratio profiles for Cl to Si, Na to Si and K to Si were compared with profiles predicted by the model. In Figure 8 the intrinsic diffusion coefficients for alkalis were adjusted. The measured ingress profiles could be fitted by increasing all diffusion coefficients by a factor of 4.5 to include the effect of cracks or other defects expected and reducing the intrinsic diffusion coefficient of the alkalis by a factor of 100 (i.e. D_{Cl} scaled by 4.5, $D_{Na,K}$ scaled by 4.5/100). The scattering of points for "Average of 3 ingress profiles (EDS)" is due to a combination of reduced measuring time and a single measuring point not being representative. The predicted ingress profiles agree with the measured (average of 200 EDS) profiles for Cl to Si, Na to Si and K to Si when the above mentioned corrections are made.
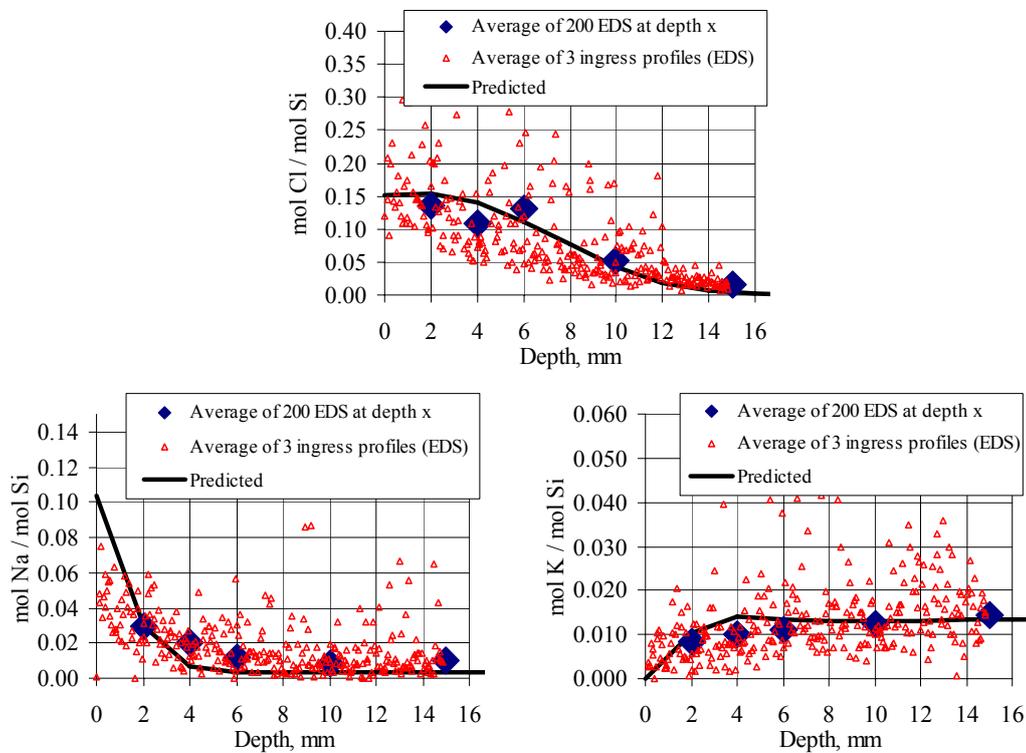

Figure 8: Measured vs. predicted profiles of Cl, Na and K after unidirectional exposure to 650 mM NaCl for 70 days at 20°C (w/p 0.45 WPC(12) paste with 1 wt. % replacement of powder

by calcite). Note; D_i for K and Na have been adjusted by 1/100 and D_i has been scaled by a factor 4.5 to account for imperfections. After [Nielsen 2004].

5. Selected observations

The applicability of the models is exemplified in the following. Based on the phase equilibria model the following observations were made:

- Chloride binding in Portland cement pastes is highly dependent on the content of alkalis; the higher content of alkalis the lower amount of bound chloride at any total content of chloride. Contrary to general agreement, the content of alumina was shown to only play a relative minor role in the overall extent of chloride binding, as the major part of chloride is bound by the C-S-H phase.
- The increased chloride binding capacity obtained by reducing the alkali content of the cement also reduces the ratio of chloride to hydroxyl ions in the pore solution[9] as long as the content of alkalis is low; $Na_2O_{eq} < 0.30$-0.35. This occurs even though the initial pH of the pore solution is also lower at these low alkali contents.
- As alkalis are transported at a much slower rate into concrete than chlorides, low-alkali Portland cements should be used in aggressive environments containing chlorides. Furthermore, owing to the minor effect of alumina on chloride binding, low-alkali low-aluminate Portland cements could arguably be recommended for aggressive marine environments providing maximum protection to both chloride transport and sulfate attack.
- At high degrees of carbonation or in cements with large amounts of limestone filler, more chloride becomes bound by aluminum bearing phases. This may be the reason why a strong influence by the C_3A content on the chloride binding of cements has been in many investigations.

6. Limitations of the models

Limitations of the phase equilibria model are among others;

- The model is restricted to Portland cement pastes with limited (see below) or without supplementary cementing materials at temperatures around $20^{\circ}C$
- The w/p of the cement paste matrix has to be high enough to ensure a residual capillary porosity at complete hydration, i.e. w/p > approx. 0.40
- The model is only valid for hydrated Portland cement pastes where the reactions proceed at a slow rate (i.e. degree of hydration is high enough), i.e. metastable or stable systems
- The Ca/Si of the paste has to be high enough to ensure the presence of both $C_{1.75}SH_4$ and CH in the stable assemblage. However, if the addition of SiO_2 is high enough to use up the CH phase, the assemblage can still be calculated as being composed of a $C_{1.75}SH_4$ and a $C_{0.8}SH_4$ (in order to ensure as many equations as unknowns), where the actual C-S-H solid solution phase is of course in reality a mixture of the two end-member phases. This would require a study of the absorption properties of this C-S-H with respect to alkalis and chloride, to be able to calculate the composition of the pore solution.

Limitations of the model for estimation of effective diffusion coefficients include;

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[9] Ratios at 0.50-0.60 are typically given as the chloride threshold value for reinforcement corrosion.

- The model does not include the the inhomogeneous pore structure of the cement paste, defects as e.g. microcracks, Interfacial Transition Zones between paste and aggregate, and tortuosity
- The model is based on the assumption of a quasi-instantaneous binding (justified for chlorides but not for sodium).

7. Conclusions

A Finite Difference Model (FDM) for simulation of the ingress of chloride and sodium/potassium in Portland cement based materials was developed taking into account a) the phase assemblage present and b) the effect of capillary porosity of the hydrated paste on the effective diffusion coefficient.

The FDM allows prediction of the (relative) performance of different types of Portland cement towards the ingress of chloride and sodium/potassium without having to carry out extensive and time-consuming experiments for calibration purposes.

Further research should be carried out to calibrate the model to chloride and sodium ingress measurements on concrete, determining the effect of imperfections. The effect of a possible layer, e.g. of carbonate or brucite, at the surface of the concrete should also be included to obtain realistic predictions.

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