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Binding of chloride and alkalis in Portland cement systems

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Abstract

A thermodynamic model for describing the binding of chloride and alkalis in hydrated Portland cement pastes has been developed. The model is based on the phase rule, which for cement pastes in aggressive marine environment predicts multivariant conditions, even at constant temperature and pressure. The effect of the chloride and alkalis has been quantified by experiments on cement pastes prepared from white Portland cements containing 4% and 12% C_3A, and a grey Portland cement containing 7% C_3A. One weight percent calcite was added to all cements. The pastes prepared at w/s ratio of 0.70 were stored in solutions of different Cl ($CaCl_2$) and Na (NaOH) concentrations. When equilibrium was reached, the mineralogy of the pastes was investigated by EDS analysis on the SEM. A well-defined distribution of chloride was found between the pore solution, the C-S-H phase, and an AFm solid solution phase consisting of Friedel's salt and monocarbonate. Partition coefficients varied as a function of iron and alkali contents. The lower content of alkalis in WPC results in higher chloride contents in the C-S-H phase. High alkali contents result in higher chloride concentrations in the pore solution.

Keywords: Phase equilibria; Chloride binding; Sodium binding; Solid solution; Modelling

1. Introduction

Increasingly, "multispecies" approaches (as in, e.g., Refs. [1,2]) are being used to improve service life prediction models for the onset of corrosion of steel reinforcement. These take into account the electrical interaction between diffusing ions and the concentration of each of these, which strongly influence the rate of diffusion of each ion in a multicomponent solution.

The rate of transport is also highly dependent on the interaction of each of the species with the solid phases in the cement paste, as well as the concentration gradient for each of the species. This appears to result in significantly higher penetration rates for chlorides than alkalis, as observed in the profiles in Ref. [3], as well as unpublished data by the present authors.

Given today's still incomplete understanding of the fundamental processes involved, chloride binding isotherms need to be measured for each new binder composition, using procedures as described in Refs. [4,5]. These procedures are time consuming and the result is highly dependent on the source of chlorides; that is, NaCl, which in contrast to $CaCl_2$, results in progressively higher levels of sodium as the chloride concentration is increased.

Models predicting the phase equilibria of cementitious binder systems, and the diffusion of each of the species in these systems would provide a powerful means of identifying the optimum binder composition in a given service environment.

Studies on the mineralogy of chemical attack (mainly from seawater) and ionic transport in Portland cement pastes, with and without supplementary cementitious materials, are presently being carried out by the present authors. A thermodynamic model for calculating the phase assemblage in Portland cement pastes was presented in Ref. [6]. The model was applied in Ref. [7] to quantify the distribution of chloride between the solid solution phase of Friedel's salt and monocarbonate, and chloride incorporated in the C-S-H phase. In the present paper, this model is developed further to include the effect of alkalis.

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2. Phase equilibria

As described in Ref. [6], the phase rule applies to all chemical systems in equilibrium. It states that the number of phases (*P*) plus the degrees of freedom (*F*) of a system must equal the number of components (*C*) at constant temperature and pressure.

A fully hydrated Portland cement paste has six major components (i.e., SiO_2, Al_2O_3, CaO, Fe_2O_3, SO_3, and H_2O) and can form a maximum of six phases (five hydrate phases and the pore solution). For a typical Portland cement paste, the phases initially formed would be [6]: $C_{1.75}$-S-H_4, calcium hydroxide, monosulfate, ettringite, iron hydroxide (FH_3), and the pore solution. Depending on the Al_2O_3/SO_3 ratio, an hydroxy-AFm phase may occur instead of ettringite, or gypsum instead of monosulfate.

In aggressive environments, concrete structures are often subjected to attack by sulfates, carbon dioxide, chloride, and alkalis. The phase assemblages which form are of course dependent on the composition of the system, in addition to temperature and pressure, regardless of whether the components have an external or internal origin. Depending on the relative content of CO_2, calcite and/or monocarbonate will be present in the stable assemblage (see Ref. [6]).

As reported in Refs. [7–10], a complete solid solution exists between monocarbonate and Friedel's salt in Portland cement pastes. The relationship between the amount of chloride incorporated in the C-S-H and chloride in the solid solution phase (expressed as fraction of Friedel's salt in the solid solution phase) was found to be strongly dependent on the iron content, as shown in Fig. 1, owing to the solid solution of iron in the C-S-H phase, reported in Ref. [6].

The presence of sodium in a hydrated Portland cement which already contains chloride must be defined by at least two additional components. The choice of Na_2O as a component is sufficiently to describe the incorporation of Na in the solid phases (essentially C-S-H), whilst both Na_2O and NaCl are needed to account for the presence of both NaCl and NaOH in the pore solution. 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 the 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.

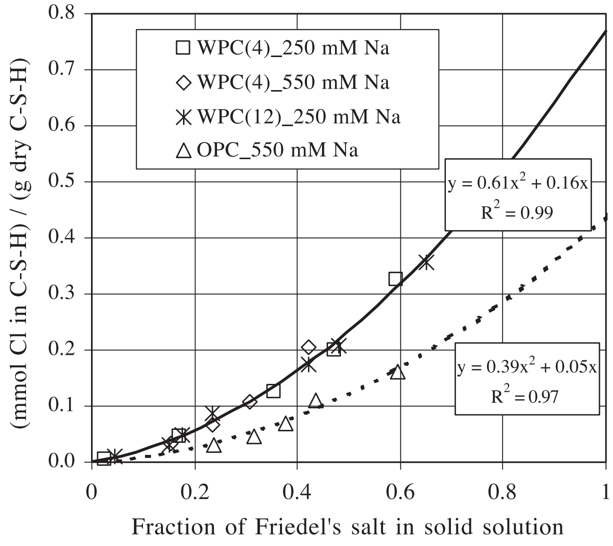

Fig. 1. Chloride content in the C-S-H vs. molar fraction of Friedel's salt in the AFm solid solution phase. Dashed curve corresponds to OPC pastes. The solid curve corresponds to the two WPCs.

Hong and Glasser [11,12] investigated the incorporation of alkalis (both sodium and potassium) up to equilibrium concentrations of 300 mM in artificially prepared C-S-H and determined the distribution ratio, R_d, defined by the concentration of sodium or potassium in the C-S-H phase divided by the concentration in the pore solution, expressed as ml/g ([mmol alkali in C-S-H/g-dry C-S-H]/[mmol alkali in solution/ml solution]). The R_d value was found to be independent of the content of alkalis in the system, but strongly dependent on the Ca/Si ratio of the C-S-H.

In aggressive environments, at least four additional components are introduced to the system, i.e., CO_2, $CaCl_2$, Na_2O, and NaCl (note that Na_2O is the only alkali considered at this stage, and that sulfate was already listed among the components in Portland cement paste).

All systems of fully hydrated Portland cement pastes exposed to aggressive marine environment have therefore at least three degrees of freedom (i.e., $P+F=C$; $7+F=10$); one degree of freedom made possible by the solid solution of Friedel's salt and monocarbonate [7], and the remaining two by the presence of alkalis. The presence of MgO is not considered in this paper and the system is therefore restricted to the following 10 components: CaO, SiO_2, Al_2O_3, Fe_2O_3, Na_2O, NaCl, $CaCl_2$, SO_3, CO_2, and H_2O.

3. Experimental

Three Portland cement pastes were examined: two white Portland cements with Bogue-C_3A contents of approximately 4% [WPC(4)] and 12% [WPC(12)], and a grey (OPC) Portland cement with a Bogue-C_3A content of 7%. The compositions of these cements are shown in Table 1.

All the pastes were prepared at a w/s ratio of 0.70 after replacement of the cement by 1.0 wt.% calcite, and cast in 2 cm^3 centrifuge tubes, sealed and kept at 20 °C for 1 month. The samples were then demoulded, crushed to 2–4 mm in size, weighed (to approximately 8.3 g) and stored in 12.5 ml solution for 5 months at 20 °C. For each cement type, the samples were stored in solutions of different $CaCl_2$ concentrations, resulting in different degrees of binding (note that a different specimen was used in each case) at constant alkali content. WPC(4) was stored at sodium contents of both 250 and 550 mM Na (by addition of NaOH to the initial solution), whilst the OPC specimens were stored in

Table 1
Composition of the Portland cements tested

Cement id.	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Na_2O	K_2O	CO_2[a]
WPC(4)	24.8	1.87	0.33	68.9	2.20	0.16	0.11	0.14
WPC(12)	23.6	4.49	0.21	65.9	2.38	0.03	0.20	0.72
OPC	21.0	4.90	3.64	65.1	3.00	0.30	0.41	0.08

Calculated Bogue composition

Cement id.	C_3S	C_2S	C_3A	C_4AF
WPC(4)	72.2	16.8	4.4	1.0
WPC(12)	51.7	28.6	11.5	0.6
OPC	59.1	15.6	6.8	11.1

[a] Determined by DTG.

solutions of 550 mM Na, and the WPC(12) specimens in 250 mM Na.

After 6 months, when the specimens were judged to have essentially attained equilibrium, the hydrated phases were examined by energy dispersive spectroscopy (EDS; at 15 keV, 25 μA, and analysis time of 40 s per point), and analysis of the solutions by titration (chloride and pH), inductively coupled plasma atomic emission spectrometry (ICP) and atomic absorption (AA) for all major elements, after removal of the solid phases by filtration.

4. Results and discussion

Table 2 shows the predicted phase assemblages for the three hydrated Portland cement pastes examined (see Ref. [6] for details of the calculations and assumptions regarding degree of hydration). Chloride was introduced to the system as a single additional component (i.e., $CaCl_2$) which resulted in the formation of Friedel's salt in solid solution with monocarbonate. EDS evidence of this solid solution can be found in Refs. [7,8] and XRD evidence in Refs. [9,13].

Table 2
Assemblages predicted for each cement paste (in wt.%)

	WPC(4)_070	WPC(12)_070	OPC_070
Assemblage no.	3	3	2
$C_{1.75}SH_4$	50.8	46.8	42.6
CH	19.2	14.4	16.4
FH_3	0.2	0.1	1.7
Pore solution	22.2	21.9	23.1
Monosulfate	–	–	6.2
Ettringite	1.9	2.8	0.8
Monocarbonate + Friedel's salt (solid solution phase)	0.4 + 0.0	8.4 + 0.0	3.7 + 0.0
Calcite	0.7	0.0	–
C_3S	1.8	1.3	1.6
C_2S	2.6	3.9	2.1
C_3A	0.1	0.3	0.2
C_4AF	0.1	0.1	1.6

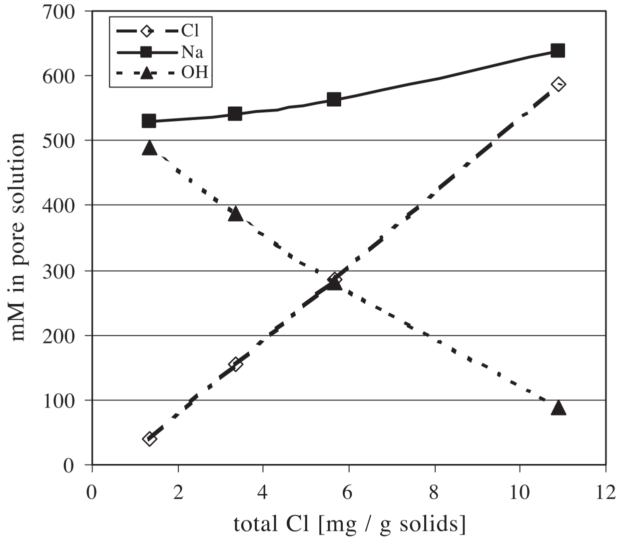

Fig. 2. Cl^-, Na^+, and OH^- concentration in the WPC(4) paste at 550 mM Na as a function of the total chloride content.

The concentrations of the major components in the solution are shown in Fig. 2 for the WPC(4) cement (at 550 mM Na) at increasing contents of total chloride. Similar trends are observed for the other cements, albeit at two different levels of Na. The Cl^- concentration increases at the expense of OH^- due to the common ion effect in which Ca^{2+} (the chloride is added to the system as $CaCl_2$) removes OH^- from solution by precipitating the more insoluble portlandite phase (Reaction 1 in Table 3). The Cl^- concentration is seen to increase slightly more than can be explained by the reduction in OH^- concentration. This discrepancy is balanced by a corresponding increase in Na^+ concentration.

Assuming that all of the Na not present in solution is bound by the C-S-H phase (a reasonable assumption based on the results of Hong and Glasser in Refs. [11,12]), the contents of Na in the C-S-H phase can be calculated as shown in Fig. 3. The Cl content bound by the C-S-H phase determined by EDS analysis is included in the same diagram. The Cl contents in the C-S-H phase can also be back calculated from the concentrations in solution in the same way as described for Na, by subtracting the chloride bound by the AFm solid solution phase (also determined by EDS analysis, see Fig. 1) to give essentially identical results. The Cl bound in the AFm phase does not affect the

Table 3
Reactions involved deduced for the binding of $CaCl_2$ in the WPC(4) paste at 550 mmol/l sodium

Reaction 1	Common ion effect	$2NaOH_{(aq)} + CaCl_{2\,(aq)} \rightarrow Ca(OH)_{2\,(s)} + 2NaCl_{(aq)}$
Reaction 2	(a) Exchange in C-S-H containing alkalis	$5\,CaCl_{2\,(aq)} + 6\,NaOH_{(C\text{-}S\text{-}H)} \rightarrow 6\,NaCl_{(aq)} + 2\,CaCl_{2\,(C\text{-}S\text{-}H)} + 3\,Ca(OH)_{2\,(s)}$
	(b) Exchange with alkali-free C-S-H	$Ca(OH)_{2\,(C\text{-}S\text{-}H)} + CaCl_{2\,(aq)} \rightarrow CaCl_{2\,(C\text{-}S\text{-}H)} + Ca(OH)_{2\,(s)}$
Reaction 3	Binding by AFm	$C_3A \cdot CaCO_3 \cdot 11H_2O_{(s)} + x\,CaCl_{2\,(aq)} \rightarrow C_3A \cdot CaCO_{3\,(1-x)} \cdot CaCl_{2\,(x)} \cdot 11H_2O_{(s)} + x\,CaCO_{3\,(s)}$

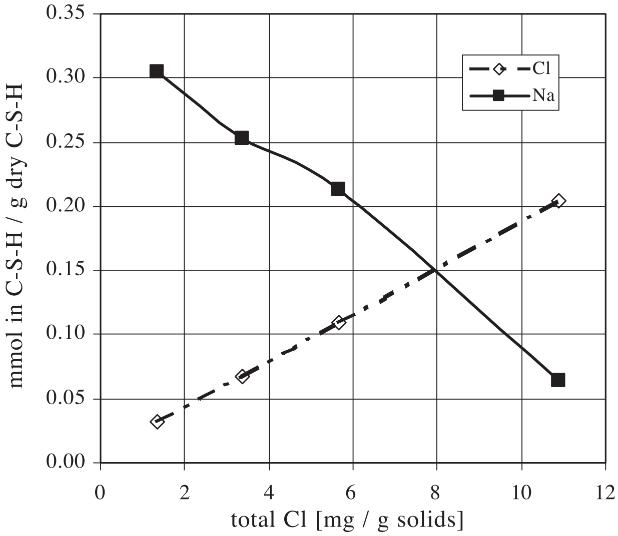

Fig. 3. Chloride and sodium content in the C-S-H, in the WPC(4) paste at 550 mM Na, as a function of the total chloride content.

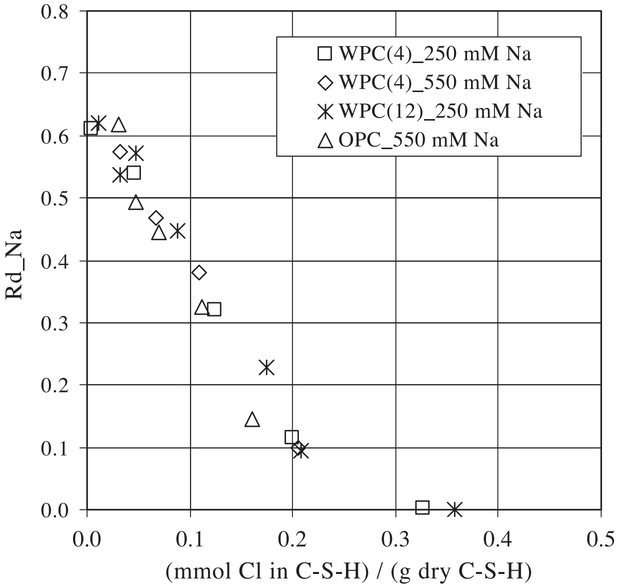

Fig. 5. Distribution ratio for alkalis, R_d, as a function of the chloride content in the C-S-H. Note: applies only for w/p 0.70 Portland cement pastes.

relationships in Figs. 2 and 3 because the $CaCl_2$ added to the system is stoichiometrically incorporated into the AFm phase as shown by Reaction 3 in Table 3. The reaction which explains the 2:3 exchange of Cl^- for Na^+ in the C-S-H phase in the WPC(4) paste at 550 mmol/l sodium is given by Reaction 2a (at low chloride contents, i.e., alkali-containing C-S-H) in Table 3.

This relationship will of course break down as the supply of Na from the C-S-H phase is exhausted. Continued addition of $CaCl_2$ leads to a 1:1 replacement of $Ca(OH)_2$ in the C-S-H by $CaCl_2$ (as shown by Reaction 2b in Table 3) and a 20:1 relation for $CaCl_2$ in solution and $CaCl_2$ in the C-S-H, deduced from similar figures for WPC(4) and WPC(12) pastes both at 250 mmol/l sodium. This explains the increase in Ca^{2+} concentration in the solution at high chloride contents shown in Fig. 4.

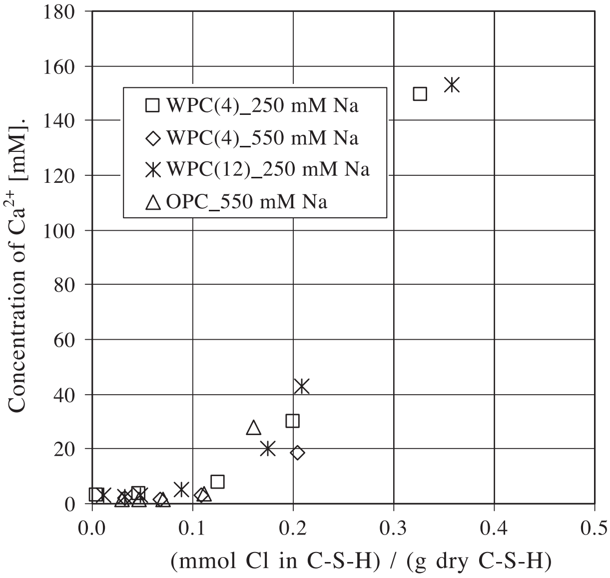

Fig. 4. Ca^{2+} concentration in the pore solution as a function of the chloride content in the C-S-H.

The data is presented in a more general way in Figs. 5 and 6, which are applicable to all comparable hydrated Portland cement pastes at water-to-powder 0.70, regardless of Na contents. Fig. 5 shows that the distribution coefficient for alkalis, R_d, between the pore solution and the C-S-H phase is not constant (as would be the case in a univariant system at constant T and P in which the sole degree of freedom corresponds to the Na content), but is inversely

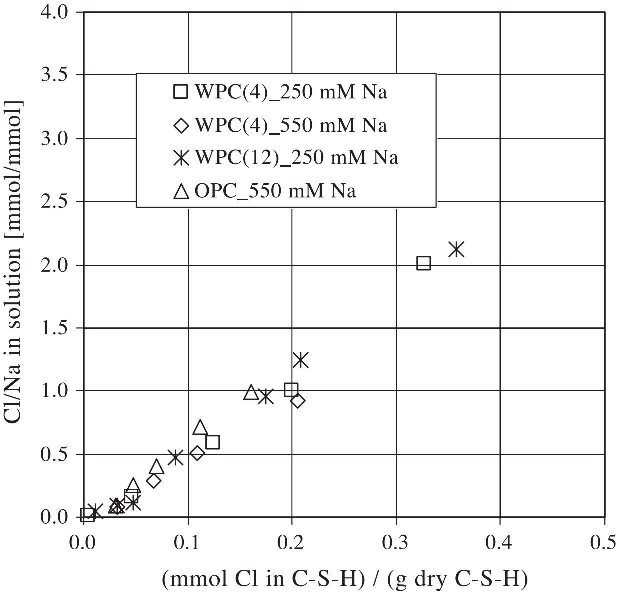

Fig. 6. Molar ratio of chloride to sodium in the pore solution as a function of the chloride content in the C-S-H. Note: applies only for w/p 0.70 pastes.

Table 4
Global complete reaction describing the binding of chloride by the C-S-H and AFm phases, and the composition of the pore solution

(1) Chloride binding in Portland cement pastes in which some Na is present in the C-S-H

$$b\cdot[C_3A\cdot CaCO_3\cdot 11H_2O]_{(s)} + a\cdot[1.75CaO\cdot SiO_2\cdot zNaOH\cdot 4H_2O]_{(s)} + ((k+1)ya+bx)\,CaCl_{2\,(aq)} + (2\times 0.83kya)\,NaOH_{(aq)}$$

$$\downarrow$$

$$2kya\,NaCl_{(aq)} + a[1.75CaO\cdot SiO_2\cdot(z-0.34ky)NaOH\cdot yCaCl_2\cdot 4H_2O]_{(s)} + kya\,Ca(OH)_{2\,(s)} + b[C_3A\cdot CaCl_{2\,(x)}\cdot CaCO_{3\,(1-x)}\cdot 11H_2O]_{(s)} + bx\,CaCO_{3\,(s)}$$

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

$$b\cdot[C_3A\cdot CaCl_{2\,(m)}\cdot CaCO_{3\,(1-m)}\cdot 11H_2O]_{(s)} + (bx+ya)\,CaCl_{2\,(aq)} + a[1.75CaO\cdot SiO_2\cdot(z/0.34k)CaCl_2\cdot 4H_2O]_{(s)}$$

$$\downarrow$$

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

In (2), for each mole of $CaCl_2$ bound by the C-S-H, $(PS/a)/75$ mol $CaCl_2$ remain in solution, where PS denotes the amount of solution in milliliters (i.e., pore solution + exposure solution, if applicable).

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

In the iron-free case (white Portland cement)
$y = 0.0601x^2 + 0.0164x$
In the iron-containing case (grey Portland cement)
$y = 0.0376x^2 + 0.0046x$

a is the content of C-S-H, in mol; b is the initial content of monocarbonate, in mol.

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 R_d, i.e., 0.65 (see the text), which is a general value, independent of water-to-powder ratio.

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

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.

proportional to the Cl content in the C-S-H phase. For all of the cements, the Na is completely removed from the C-S-H phase at a Cl content in the C-S-H phase of 0.24 mmol/g dry C-S-H. Fig. 6 shows the distribution of Cl between the pore solution and C-S-H phase for the pastes studied.

For the calculations carried out in this work, it was assumed that the part of the water in the C-S-H structure held by a weaker binding strength (see Ref. [6]), corresponding to 19 mass % of the saturated phase, was not available for the solution of ions. This led to R_d values close to 0 for Cl contents in the C-S-H higher than approximately 0.24 [mmol/g dry C-S-H]. If, on the other hand, it was assumed that this water did form part of the pore solution, negative values of R_d (approximately -0.20) would have been obtained, which is physically impossible. It is the authors' view that this so-called weakly bound water is not different from the remaining water bound by the C-S-H and is simply an artifact of the methods by which it is determined.

It should be noticed that the results presented in Figs. 2, 3, 4, 5, and 6 are dependent on the amount of solution relative to the solid phases. Only the distribution ratio for alkalis in the chloride free case, R_d of 0.65, is a global value, independent of the amount of solution. By further treatment of the data in Figs. 5 and 6, the overall global reactions taking place in hydrated Portland cement pastes upon addition of chloride were deduced, and are presented in Table 4.

The model can be used to predict the phase assemblage, including contents and compositions of the phases present in any Portland cement paste at equilibrium, at any known total alkali and chloride content, solely on the basis of the chemical composition of the system. As a first approximation, potassium can be assumed to behave similarly to sodium, which was observed by Hong and Glasser [11]. Fig. 7 illustrates the values measured for the WPC(4) pastes at 250 and 550 mmol/l sodium compared to those predicted by the described model (i.e., using the reactions in Table 4). The model was applied to chloride binding data available in the literature (see Ref. [14]) where excellent agreement was found between the mea-

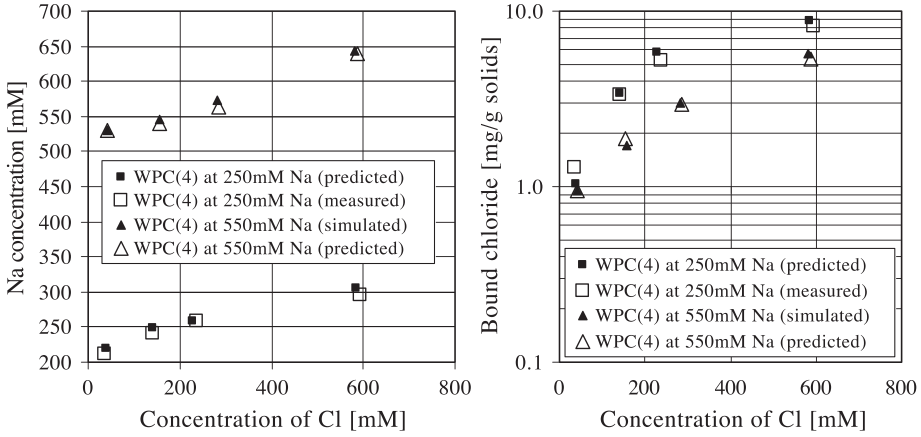

Fig. 7. Comparison between the values measured and those simulated according to the reactions in Table 4, for the pastes WPC(4) at both 250 and 550 mmol/l Na.

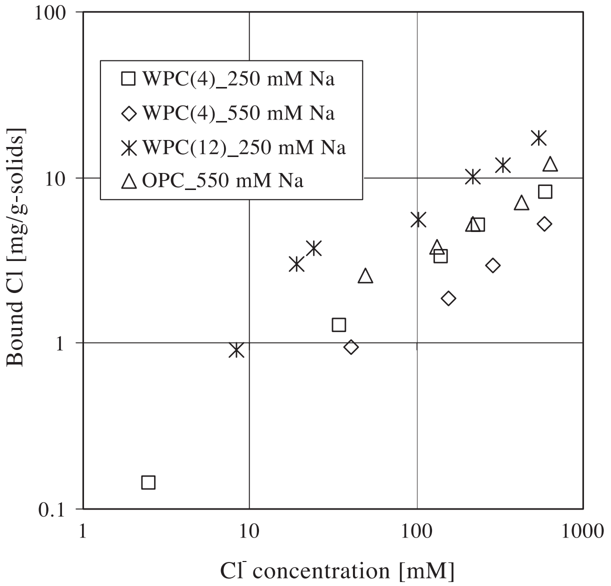

Fig. 8. Chloride binding isotherms determined for the cement pastes examined. Each isotherm is measured at a constant equilibrium concentration of Na^+.

sured and predicted results from both absorption and desorption determinations.

In carbonate-free systems (which do not exist in real concrete), the same type of binding is expected, as the monosulfate phase is likely to form a similar solid solution with Friedel's salt. This hypothesis is presently being tested. Furthermore, the addition of supplementary cementitious materials, such as silica fume, metakaolin, and slag, will not affect the model, as long as $Ca(OH)_2$ is still present in the system, or where the C-S-H is not decalcified by leaching or attack by $MgSO_4$.

Conventional chloride binding isotherms for same specimens described above are shown in Fig. 8 at two different levels of Na^+ concentration in the pore solution [250 and 550 mM for WPC(4), 250 mM for WPC(12), and 550 mM for OPC].

These concentrations are typical for the normal range of alkalis in the pore solution in normal concretes [except for WPC(4) at 550 mM Na^+]. It is observed that the binding of chlorides in WPC(4) paste at 250 mM Na^+ is similar to that in the OPC paste, although the content of Al_2O_3 is approximately three times higher in OPC. The WPC(12) paste at 250 mM Na^+ has the greatest chloride binding over the range of chloride contents studied, although it has a slightly lower content of Al_2O_3 than OPC. The maximum binding capacity of the AFm phases in the OPC cement is predicted to be slightly higher, but this is of little value in Portland cements containing alkalis given that the chloride concentration of seawater rarely exceeds 600 mM Cl^- (given as the average chloride concentration in seawater in Ref. [15]), hindering thereby the exhaustion of the binding capacity by aluminate phases.

5. Conclusion

A thermodynamic model for calculating the phase assemblage and the pore solution composition in fully hydrated Portland cement pastes has been presented. The model describes the distribution of alkalis and chloride in the solid phases and the pore solution, predicted from the chemical composition of system. The model can be used to predict the performance of different types of Portland cement under different conditions of exposure.

Alkalis have a negative impact on the binding of chlorides because they increase the concentration of chlorides in solution.

The absence of iron in white Portland cement is beneficial to chloride binding owing to significant increase in the content of Cl bound by the C-S-H phase compared to conventional Portland cement.

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