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Chloride Binding Capacity of Various Hydrated Cement Paste Systems

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The interaction mechanisms of the cement paste hydration products with chloride were investigated for various systems. Test parameters included water/binder ratio (0.25 and 0.45), type of cement (ASTM type I, III, and V), use of silica fume (6%), and chemical composition of the chloride solution. Powdered cement paste samples were immersed in solutions of different chloride concentrations. The total amount of bound chlorides was determined by measuring the equilibrium chloride concentration of the solution after 3 weeks of immersion. The chemical interaction of chlorides with the hydrated cement paste was also studied by X-ray diffractometry. Test results show that the total amount of bound chlorides increases with the chloride concentration of the solution. This nonlinear relationship can be represented best by a Freundlich isotherm. When expressed on a unit mass of cement gel basis, the total amount of bound chlorides was found to be independent of the water/binder ratio and the type of binder in all cases but one. The chloride binding capacity and the formation of chloroaluminates appear to be attributable not only to the tricalcium aluminate content but also to the total aluminate content of the cement. The use of calcium chloride instead of sodium chloride, as well as the use of a lime solution instead of an alkaline solution, increases the amount of bound chlorides. ADVANCED CEMENT BASED MATERIALS 1997, 6, 28–35. *© 1997 Elsevier Science Ltd.*

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[illegible]ith the increasing use of deicing chemicals during winter roadway maintenance operations and the resulting durability problems, the penetration of chloride ions in concrete structures has been the subject of a great deal of research [1–10]. Most studies have emphasized the complexity of the problem, which is influenced by numerous parameters such as the water/binder ratio, the type of coexisting cations, and the interaction of chlorides with the cement paste hydration products.

Although several aspects of the problem still remain to be clarified, significant progress has been made in understanding the mechanisms of chloride interaction. For instance, it is now well known that chlorides can react with the unhydrated aluminate phases to form new compounds such as calcium monochloroaluminates (or Friedel's salt), calcium trichloroaluminates, and chloroferrite hydrates. Recent studies have also clearly established that chlorides can also chemically and physically interact with the calcium silicate hydrates. In his study of the influence of $CaCl_2$ on the C_3S hydration mechanisms, Ramachandran [1] distinguished three possible types of interaction. According to the author, chlorides can either be present in a chemisorbed layer on the hydrated calcium silicates, penetrate the C-S-H interlayer spaces, or be intimately bound in the C-S-H lattice. The ability of C-S-H to bind chlorides was later confirmed by Beaudoin et al. [2], who worked on synthetic systems that had first been cured and then immersed in chloride solutions.

Over the years, numerous reports have indicated that the nature and intensity of the chloride/cement paste interaction are directly influenced by a wide range of parameters such as the type of binder and the nature of the coexisting cation [1–10]. Recent investigations have also clearly established that the interaction mechanisms are directly affected by the chloride concentration of the pore solution [11–13]. According to these reports, the amount of bound chlorides (which refers to the total amount of chlorides both chemically bound and physically adsorbed to the hydration products) increases with an increase in the chloride concentration of the surrounding solution.

From an engineering point of view, the nonlinearity of the chloride binding phenomenon is of significant importance. For instance, it has been established that the nonlinear nature of the problem has to be taken into account in any reliable prediction of the penetration of

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chlorides in concrete structures [14-16]. It should also have a significant influence on the modeling of the reinforcing steel corrosion of concrete since only the fraction of chlorides free in the pore solution participate in the corrosion process.

This report presents the results of an experimental study specifically designed to determine more quantitative information on the chloride interaction mechanisms. The investigation was carried out as part of a more comprehensive research program aimed at studying the long-term durability of high-performance concrete structures exposed to chloride solutions [17].

Test Program

The test program was divided into two distinct parts. In the first test series, the influence of the mixture characteristics on the hydrated cement paste chloride binding capacity was investigated. Test parameters included the water/binder ratio (0.25 and 0.45), the type of cement (ASTM type I, III, and V), and the use of silica fume (with and without). Interaction mechanisms were investigated using a binding isotherm technique. All samples were immersed in lime saturated solutions prepared at different chloride concentrations. X-ray diffractometry was used to identify new chloride based compounds.

The objective of the second series of tests was to study the effect of the chloride solution composition on the interaction mechanisms. The parameters included the composition of the solution (lime solution or alkaline solution) and the nature of the chloride salt (NaCl and $CaCl_2$). In this second series of tests, only the reference mixture (0.45 water/binder ratio, ASTM type I cement) was tested.

Materials and Experimental Procedures

Materials and Mixture Characteristics

Since previous investigations had indicated that the presence of paste/aggregate transition zones had very little influence on chloride binding [10,13], it was decided to limit this study to neat cement paste mixtures. Overall, five different mixtures were prepared for this investigation.

Two 0.25 water/binder ratio pastes were prepared with an ASTM type III cement. Silica fume (6% of the total binder mass) was added to one of these two mixtures. A melamine based superplasticizer was used in both cases. The dosage was fixed at 2.1% of dry material by mass of cement. An ASTM type I cement was used in the preparation of two 0.45 water/binder ratio mixtures. Silica fume (6% of the total binder mass) was added to one of these two mixtures. An ASTM type V cement (low C_3A content) was used for the fifth mixture (0.45 water/binder ratio). Demineralized water was used in the preparation of all mixtures. The chemical analyses of the three cements are given in Table 1. The composition of the five mixtures is given in Table 2.

TABLE 1. Chemical and mineralogical compositions of cement

Chemical Analysis (%)	ASTM I	ASTM III	ASTM V
Silicon dioxide (SiO_2)	20.1	20.5	22.3
Aluminum trioxide (Al_2O_3)	3.9	4.0	3.5
Ferric trioxide (Fe_2O_3)	1.7	1.8	4.4
Calcium oxide (CaO)	63.8	64.7	63.9
Magnesium oxide (MgO)	2.2	2.3	1.4
Sulfur trioxide (SO_3)	3.5	3.3	2.2
Potassium oxide (K_2O)	0.4	0.3	0.7
Sodium oxide (Na_2O)	0.3	0.4	0.2
Titanium dioxide (TiO_2)	0.2	0.2	0.2
Manganese oxide (MnO)	0.1	0.1	0.1
Bogue composition (%)			
C_2S	68.7	68.7	54.9
C_3S	5.8	6.9	22.5
C_3A	7.4	7.7	1.8
C_4AF	5.1	5.4	13.3
Physical properties			
Blaine (cm^2/g)	4620	5350	3800

Reagent grade sodium chloride and calcium chloride salts were used to prepare the various chloride solutions used in this study. Reagent grade calcium oxide was used in the preparation of the lime saturated solutions. All alkaline solutions were prepared with reagent grade sodium hydroxide and potassium hydroxide. All solutions were prepared with demineralized water.

Mixture Preparation and Curing

To produce homogeneous mixtures, all pastes were prepared in a high-speed mixer. Cylindrical specimens (diameter 9.5 cm, height 20 cm) were cast in plastic molds. The molds were sealed and rotated for the first 24 hours to prevent any segregation of the paste. At the end of this period, the specimens were demolded and immersed in a saturated lime solution for a minimum period of 1 year.

TABLE 2. Mixture characteristics

Mixture	Cement Type	Silica Fume (% of total mass of binder)	Water/Binder
P25Q3	Type III	0	0.25
P25Q3SF	Type III	6	0.25
P45Q1	Type I	0	0.45
P45Q1SF	Type I	6	0.45
P45Q5	Type V	0	0.45

Experimental Procedures

Chloride binding isotherms were determined according to the procedure developed by Tang and Nilsson [13]. Paste samples were first ground to pass a 2-mm sieve. The powdered samples were vacuum dried for a minimum period of 4 days and then kept at a relative humidity of 11% (over a LiCl salt) for 7 days. The powdered samples (approximately 20 g each) were then immersed in solutions of different chloride concentrations. The cups containing the crushed samples and the chloride solutions were sealed (to prevent any evaporation of the solution) and stored at 21°C for a minimum period of 3 weeks. At the end of the immersion period, the new chloride concentration of the solution was determined by means of potentiometric titration using a silver nitrate electrode.

According to Tang and Nilsson [13], only 7 days of immersion are generally sufficient to reach the equilibrium between the solid and the solution. To verify this assumption, additional measurements were made on selected samples that were kept immersed in chloride solutions for several months. Data clearly confirmed that the equilibrium had been achieved after a 3-week exposure period.

For the first series of tests, ten different saturated lime solutions were prepared at different sodium chloride concentrations (1, 3, 5, 7, 10, 15, 20, 25, 30, and 40 g/L of chloride ions), and the volume of solution in each cup was fixed at 50 ml. After the 3-week exposure period, the powdered paste samples of each of the five mixtures in contact with the 0, 1, 5, 10, and 20 g/L chloride solutions were vacuum dried and analyzed by X-ray diffractometry. X-ray diffraction data were collected using Co radiation with a Siemens D5000 diffractometer operating at 40 kV and 30 mA. A range of 6° to 52° (2θ) was scanned at step intervals of 0.02° (2θ) using a step scan time of 3 seconds.

The X-ray diffraction results were analyzed qualitatively to determine if new chloride based compounds had been formed during the period of exposure to the chloride solutions. It should be emphasized that X-ray diffraction results are not truly quantitative because the intensity of the peaks is not only a function of the quantity of the crystalline phase present in the sample, but is also influenced by the orientation of the crystals and the degree of compaction of the powdered sample.

In the second series of tests, the influence of the chemical composition of the chloride ion solution was first studied by replacing the saturated lime solution with an alkaline solution (1 g/L NaOH + 4.65 g/L KOH). In this case, chloride ions were added as NaCl. The influence of the chloride salt was also studied by replacing NaCl with $CaCl_2$. These tests were conducted with a saturated lime solution. The chloride concentrations used to study the influence of the chemical composition of the chloride solution on the binding capacity were the following: 1, 3, 5, 7, 10, 15, 20, 25, 30, 40, and 60 g/L of chloride ions. In this second series of tests, the volume of solution in each cup was fixed at 100 ml.

The amount of bound chlorides was calculated according to eq 1:

$$C_b = \frac{(C_0 - C_1)V}{W} \tag{1}$$

where C_b = bound chloride content (mg Cl^-/g sample); C_0, C_1 = initial and equilibrium chloride concentrations (mg/L); V = volume of the chloride solution (L); and W = sample weight (g).

The amount of bound chlorides can also be expressed on a unit mass of cement gel basis. The total cement gel content of a given mixture can be estimated according to the eq 2 [13]:

$$W_{gel} = \frac{(1 + W_n^0)f_c\alpha}{1 + W_n^0 f_c\alpha} W \tag{2}$$

where W_n^0 = constant equal to 0.25 for ordinary Portland cement (OPC) mixtures and 0.24 for silica fume mixtures; α = degree of hydration; and f_c = cement content of the mixture in mass (f_c = 1 for neat cement pastes).

Degree of hydration values were calculated on the basis of nonevaporable water content data obtained from thermogravimetric analyses (TGA). Loss of weight between drying at 105°C and 1000°C was considered to represent the nonevaporable water content. All thermal analyses were performed using a Perkin-Elmer thermobalance on crushed samples that had been previously vacuum dried. Generally, 30-mg samples were heated, in a nitrogen atmosphere, at a rate of 10°C/min. Corrections were made to account for the unhydrated cement loss on ignition.

In all calculations of degree of hydration (α) and cement gel content, the value of W_n^0 was fixed at 0.25 for OPC mixtures (i.e., it was assumed that 0.25 g of water is required to fully hydrate 1 g of cement). Such a value is in good agreement with the ^{29}Si nuclear magnetic resonance measurements of Justness et al. [18] and Sellevold and Justness [19]. For the silica fume pastes, the value of the constant was fixed at 0.24. According to the data reported by Justness et al. [18], Sellevold and Justness [19], Cheng-Yi and Feldman [20], and Atlassi [21], the hydration of silica fume pastes tend to bind less water.

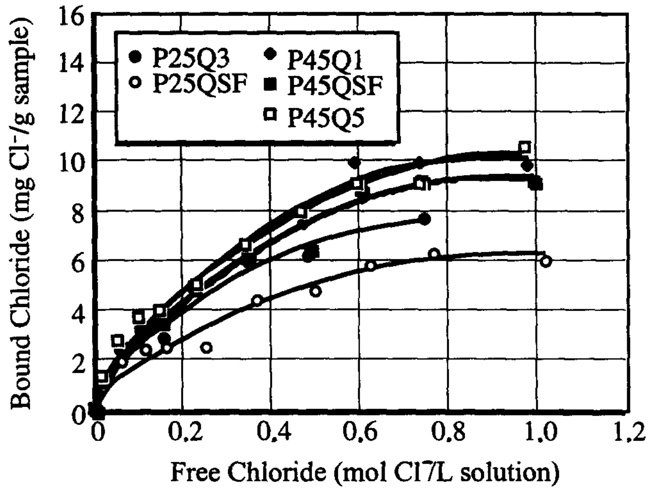

FIGURE 1. Influence of mixture characteristics on chloride binding capacity.

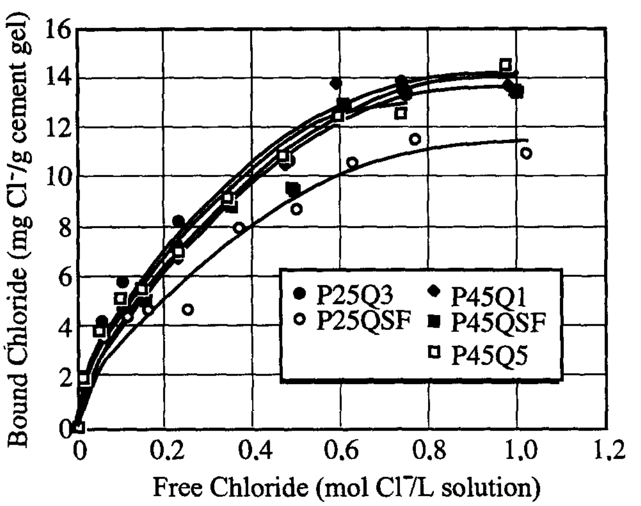

FIGURE 2. Chloride binding isotherm expressed on a unit mass of cement gel basis.

Test Results

Influence of the Mixture Characteristics

The chloride binding isotherms for the five neat paste mixtures are presented in Figure 1. The amount of bound chlorides (C_b) (expressed on a unit mass of sample basis) is given as a function of the equilibrium free chloride concentration (C_f). The plots of Figure 1 show that the total amount of bound chlorides increases with the chloride ion concentration of the solution. It can also be clearly seen that the relationship is not linear. The nonlinearity of the chloride binding isotherm is particularly pronounced for chloride concentrations in the 0 to 0.8 mol/L range.

Results of Figure 1 also indicate that, when the amount of bound chlorides is expressed on a unit mass of sample basis, parameters such as water/binder ratio and silica fume appear to have a significant influence on binding mechanisms. The 0.25 water/binder ratio pastes clearly tend to bind significantly less chlorides than the 0.45 water/binder mixtures. The use of silica fume also tends to reduce markedly the total amount of bound chlorides.

The amount of bound chloride can also be expressed on a unit mass of cement gel basis. The cement gel contents (W_{gel}) calculated according to eq 2 are given in Table 3. The nonevaporable water contents (W_n) obtained from the TGA analyses and the calculated degree of hydration values are also included in the table. As can be seen, the various paste mixtures, particularly the low water/binder ratio samples, are not fully hydrated.

TABLE 3. Degree of hydration values and cement gel contents

Mixture	W_n (g/g ignited)	Degree of Hydration (%)	W_{gel} (g/g of sample)
P25Q3	0.13	52	0.57
P25Q3SF	0.11	47	0.54
P45Q1	0.17	67	0.72
P45Q1SF	0.15	62	0.68
P45Q5	0.17	68	0.72

The recalculated binding isotherms are presented in Figure 2. When expressed on a unit mass of cement gel basis, the total amount of bound chlorides appears to be independent of the water/binder ratio and the type of binder in all cases but one (mixture P25QSF). According to Figure 2, the cement gel content of a given system is clearly the key parameter that controls the binding mechanisms. Similar results were found by Tang and Nilsson [13].

It should be emphasized that the expression of the amount of bound chlorides on a unit mass of cement gel basis for both the OPC and the blended cement pastes is not rigorously correct. In doing so, one tacitly assumes that the cement gel composition is similar for both series of mixtures. Such an assumption is obviously false, considering that silica fume is known to decrease the portlandite content of the cement gel and the Ca/Si ratio of the C-S-H [18–20]. The relevant data for silica fume cements are too scanty and uncertain to allow any reliable expression of the hydration stochiometry. However, on the hypotheses that all the silica fume has reacted[1] and that the Ca/Si of the new C-S-H formed does not fall below 1, the C-S-H contents of the two blended cement pastes should not differ by more than 10% from the value used in the calculation of the

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[1] Such an assumption is in good agreement with the ^{29}Si nuclear magnetic resonance measurements of Justness et al. [19,20], which indicate that silica fume is an extremely reactive material even in very low water/binder ratio systems.

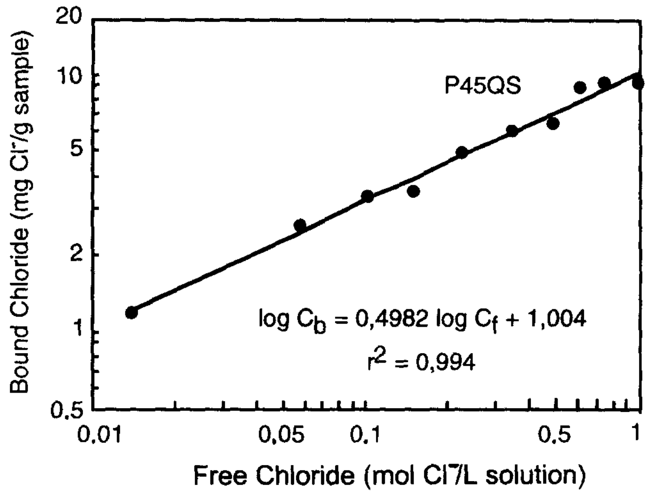

FIGURE 3. Typical Freundlich isotherm for the P45Q1SF mixture.

binding isotherms of Figure 2. In that respect, the curves of Figure 2 can be considered as good approximations of the "true" binding isotherms.

As can be seen in Figures 1 and 2, the chloride binding isotherms of mixture P45Q1 (made of a cement containing 7.4% C_3A) are similar to those of mixture P45Q5 (made of the type V cement with only 1.8% of C_3A). Both series of curves remain very close together whatever the chloride concentration of the external solution.

Binding Isotherm Modeling

Chloride binding isotherms can be represented by a Freundlich isotherm for high concentrations (>0.01 mol/L of chloride ions) [12,13,16]:

$$\log C_b = a \log C_f + b \qquad (3)$$

where a and b are the adsorption constants. A typical Freundlich isotherm is presented in Figure 3. The values of the constants a and b and the correlation coefficient (r^2) for each mixture are presented in Table 4. The results listed in Table 4 tend to confirm the conclusions of Tang and Nilsson [12,13], and Bigas [16]. In all cases, the correlation coefficients are >98%.

TABLE 4. Freundlich isotherm data

Mixture	a	b	r^2
P25Q3	0.4642	0.936	0.985
P25Q3SF	0.4772	0.814	0.981
P45Q1	0.5133	1.048	0.992
P45Q1SF	0.4982	1.004	0.994
P45Q5	0.4757	1.037	0.997

X-Ray Diffraction Analysis

The X-ray diffraction diagrams of all mixtures are presented in Figure 4. As can be seen, a distinct monochloroaluminate peak [13° (2θ)] can be observed on many diagrams. Although X-ray diffractometry does not provide any reliable quantitative information, the technique is extremely sensitive. The intensity of the main monochloroaluminate peak appears to increase with an increase of the chloride concentration of the external solution. Peaks associated with other chloroaluminate and chloroferrite phases were generally indistinct and formed no consistent pattern. Such a predominance of monochloroaluminate peaks is in good agreement with data reported by Jensen and Pratt [22].

According to Figure 4, monochloroaluminate formation appears to be influenced by both the water/binder ratio and the use of silica fume. The height of the main chloroaluminate peak decreases with the water/binder ratio. The intensity of the chloroaluminate peak is also systematically reduced (to become even undetectable in certain cases) when silica fume is present in the mixture.

It should be emphasized that distinct monochloroaluminate peaks were detected for mixture P45Q5 made of a low C_3A cement. Furthermore, the amount of monochloroaluminates formed in this mixture does not seem to be significantly different from that of mixture P45Q1, which was prepared using an ASTM type I cement with a much higher C_3A content.

Influence of the Chloride Solution Composition

The chloride binding isotherms for mixture P45Q1 are presented in Figure 5. These results clearly show the importance of the chemical composition of the chloride solution on the chloride binding mechanisms. The total amount of bound chlorides is much higher for the lime saturated solution than for the alkaline solution (NaOH + KOH).

The nature of the chloride salt also appears to have a very significant influence on the chloride binding capacity. As can be seen in Figure 5, the amount of bound chlorides is clearly enhanced for the samples immersed in a calcium chloride solution. The influence of the associated cation is particularly marked in the low chloride concentration range.

Discussion

The isotherms shown in Figures 1, 2, and 5 clearly confirm that the concentration dependency and the nonlinear nature of the hydrated cement paste chloride binding capacity. The significant influence of the latter characteristic of the phenomenon on the chloride ion transport mechanisms has been previously discussed in

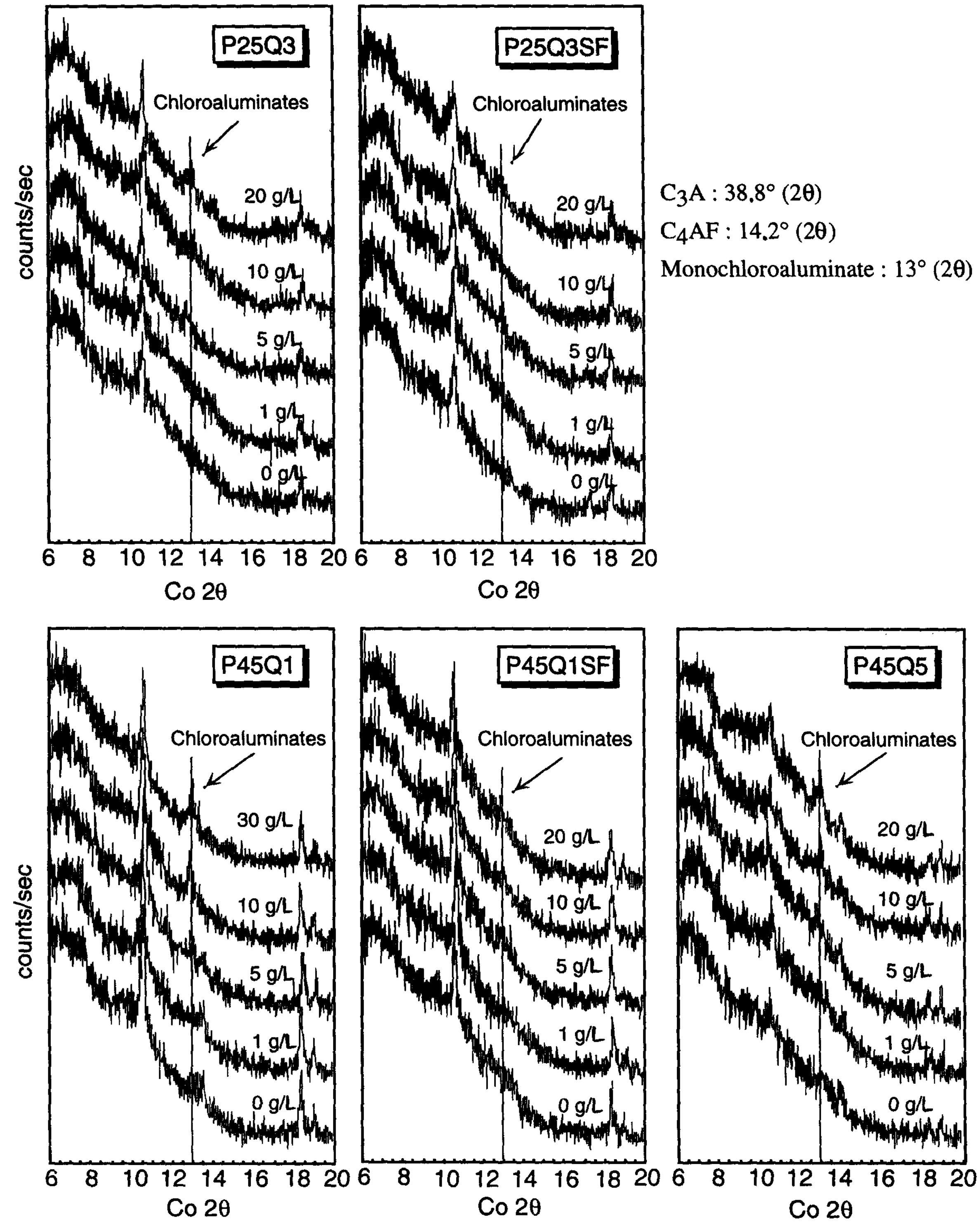

FIGURE 4. X-ray diagrams for the five mixtures after 3 weeks of exposure to the chloride solutions.

detail [14–16] and should be taken into account in any reliable prediction of the chloride ion ingress in concrete structures. Any prediction made without taking into account the chloride binding capacity can significantly overestimate the penetration depth of chloride ions.

As previously mentioned, chlorides can interact with various hydrated and unhydrated phases of the cement

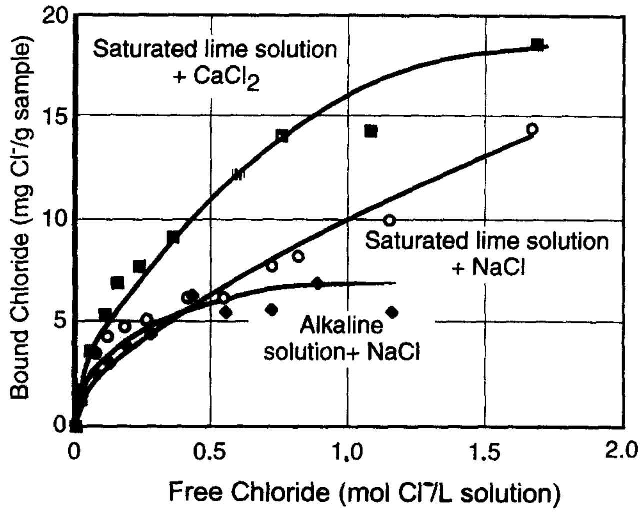

FIGURE 5. Influence of the solution chemical composition on the chloride binding isotherms.

paste. The fact that the amount of bound chlorides was found to be predominantly influenced by the cement gel content and the reduced amount of chloroaluminates detected in the low water/binder ratio pastes tend to emphasize the significant influence of the C-S-H gel on the binding mechanisms. When compared to the unhydrated cement, the cement gel has a much higher specific surface. It therefore offers more adsorption sites to the chloride ions. Since most of the specific surface of the cement gel comes from the C-S-H, it can be reasonably assumed that they directly affect the chloride binding mechanisms.

In that respect, the small influences of the water/cement ratio and the cement type are consistent with the conclusions of previous studies. Both parameters were found to alter the hydration kinetics of the cement paste. However, it has been established that, for a given degree of hydration, they do not significantly influence the cement gel C-S-H content [18,19].

As can be seen in Figure 2, the addition of 6% silica fume did not markedly influence the binding capacity of the 0.45 water/binder mixture. The small difference noted between the isotherm of mixture P45Q1 and that of mixture P45QSF is insignificant with respect to the experimental precision. These results are in contradiction with previous observations in which silica fume was found to reduce the cement paste binding capacity [3,5]. If one accepts that the binding mechanisms are mainly controlled by the C-S-H gel, the small influence of the silica fume is also surprising. The presence of silica fume has been found to reduce the Ca/Si ratio of the C-S-H [18,19,23]. Such a reduction should alter the surface characteristics of the gel and reduce the number of adsorption sites [3,24]. It is possible, however, that the low replacement rate (6%) and the high degree of hydration of the mixture have both contributed to attenuate the effect of the silica fume on the C-S-H surface characteristics.

The influence of the silica fume on the binding capacity of the low water/binder ratio paste is in better agreement with the conclusions of previous studies [3,5]. In that specific case, it is probable that the low degree of hydration of the mixture has enhanced the influence of the silica fume on the mean Ca/Si ratio of the C-S-H. As previously mentioned, silica fume is a very reactive material even in low water/binder ratio systems [18,19].

The relatively low influence of the cement C_3A content on the binding capacity as well as on the chloroaluminate formation of mature pastes confirms the conclusions of Arya et al. [7]. According to these authors, the C_3A content is a significant parameter only when chlorides are introduced at the time of mixing. In mature pastes, much of the C_3A has already reacted with the sulfates, and the amount of unhydrated C_3A is thus markedly reduced. The very distinct monochloroaluminate peak detected for mixture P45Q5 (low C_3A content) also tend to support the conclusions of Theissing et al. [6] and Glasser et al. [9] that the formation of chloroaluminates in well-cured cement systems is probably affected by the total aluminate content of the cement rather than solely being a function of the cement C_3A content.

The marked reduction of the amount of chloroaluminates formed in the low water/binder ratio systems is in good agreement with the data of a previous project in which disks of paste were immersed for a 12-month period in a chloride solution [25]. Chloroaluminate crystals were readily detected in the mixture having a water/binder ratio of 0.38, whereas they were never observed in the 0.25 water/binder ratio paste. These results emphasize the complexity of the chloroaluminate formation mechanisms, which are not solely function of the cement composition but can also be affected by the pore structure of the system (which control the accessibility of chlorides to the reaction sites) and the pore solution chemistry (which can influence the chloroaluminate solubility).

The marked influence of the solution chemical composition on the binding mechanisms is in good agreement with the results of previous studies. For instance, the fact that the total amount of bound chlorides was found to be much higher for the lime saturated solution than for the alkaline solution (NaOH + KOH) tend to confirm the assumption of Tritthart [8] that chloride ions are mainly competing with the hydroxide ions for the adsorption sites. The strong influence of the associated cation also tend to support the conclusions of Arya et al. [7], who reported a significant increase in binding for calcium chloride and magnesium chloride solutions in comparison with sodium chloride solutions. The influence of the associated cation has also been reported by Suryavanshi et al. [26]. The nature of the associated cation probably has a predominant influence on the chloroaluminate solubility and the accessibility of chloride ions to the adsorption sites.

Conclusion

The test results presented confirm the concentration dependency and nonlinear nature of the hydrated cement paste chloride binding capacity.

For a given chloride solution, the amount of bound chlorides appears to be predominantly influenced by the cement gel content of the mixture. When expressed on a unit mass of cement gel basis, the total amount of bound chlorides was found to be independent of the water/binder ratio and the type of binder in all cases but one.

The total amount of bound chlorides and the formation of chloroaluminates are probably more related to the total aluminate content (C_3A + C_4AF) than to the C_3A content.

The chemical composition of the chloride solution also has a significant influence on the binding capacity. The use of $CaCl_2$ instead of NaCl, as well as the use of a lime solution instead of an alkaline solution, increases the amount of bound chlorides.

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