

CHLORIDE BINDING IN CEMENT PASTE



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The purpose of this study was to map out the influence of a number of factors on the capacity of cement paste to bind chloride. The results show that the cement type, mineral additives (silica fume and fly ash) and chemical admixtures influence the ability of the paste to bind chloride. It is not, on the other hand, the C_3A content of the cement which appears to be the decisive factor. Instead, differences in chloride binding can probably be related to the cement's total concentration of C_3A and C_4AF , its specific surface, its chemical composition and, consequently, the composition of the pore solutions. Experiments also showed that the concentrations of the surrounding solution of Cl^- , OH^- and SO_4^{2-} has a significant effect on the chloride binding capacity.

Keywords: Chloride binding, cement type, silica fume, fly ash, pore solution composition

1 BACKGROUND

Chlorides occur in concrete bound in hydration products, adsorbed on pore walls and as free ions in the pore solution. The distribution between free and bound chlorides is significant for the risk of reinforcement corrosion. This is because only the free chloride ions can cause corrosion. Chlorides bound in the hydration products are thus "harmless".

A number of factors determine how the total chloride concentration will be distributed amongst free and bound ions. Many references in the literature indicate that the composition of the cement, particularly the C_3A content, is of major significance. The reason for this is that an insoluble complex, Friedl's salt ($3CaO \times Al_2O_3 \times CaCl_2 \times 10H_2O$) in which chlorides are bound, is formed. Exchange reactions can probably take place so that other ions in solution, for example SO_4^{2-} and OH^- , can compete with chloride ions for space in the complex. There are many indications that cement components other than C_3A can also bind chloride chemically.

With regard to the quantity of physically adsorbed chloride, the specific surface of the cement is probably of major significance.

It must also be borne in mind that the chloride concentration of the surrounding solution affects the chloride binding capacity since it is, throughout the entire process, a question of equilibrium between free and bound chlorides. The higher the chloride concentration of the solution, the more chloride (counted as a percentage of the cement weight) can be bound. The quantity of bound chloride also depends on the salt cation, see /6/, /7/, /8/.

The chloride binding capacity affects the corrosion process both when chloride is mixed in the fresh concrete and when chloride penetrates the concrete from the outside. When chloride is mixed in the concrete from the beginning, equilibrium will be established between free and bound chlorides. Although the mechanism for depassivating the steel is not completely known, we do know that the risk of corrosion increases if the ratio between chloride and hydroxide in the pore solution is high. A high chloride binding capacity, in other words a low concentration of chloride in the pore solution, is thus an advantage.

In those cases in which the chlorides penetrate the concrete from the surface, the chloride binding capacity will affect the rate of penetration. The hydration products of the cement paste can be likened to a "container" which is gradually filled in pace with the penetration of the chlorides. The more room there is in this container (the greater the chloride binding capacity) the longer the time it will take before the chloride concentra-

tion at the steel is sufficiently high for corrosion to start. This procedure almost certainly applies to chloride transport both via diffusion and capillary suction. A few simple experiments carried out at CBI have shown that the chloride binding progresses very rapidly. Here, too, a high chloride binding capacity is thus an advantage from the durability point of view.

The capacity of the cement paste to bind chloride is thus one factor amongst several others, which determine whether reinforcement corrosion will start or not, how long a time it will take before the attack starts and the rate at which the attack will proceed. Amongst the other important, controlling factors the following are worth noting:

- transport rate for chlorides
- threshold value for chlorides
- access to oxygen
- access to moisture

Several of these parameters are at present being studied in CBI's ongoing research project, P37. This report presents the results achieved so far concerning chloride binding. The purpose of this part investigation was to map out the influence of a number of factors on the chloride binding capacity: The cement brand, mineral additives (silica fume and fly ash) and chemical admixtures (lignosulphonate, melamine, naphthalene).

The composition of the solution in which the samples are exposed has also been varied with regard to the concentration of Cl^- , SO_4^{2-} and OH^- .

A new test method developed at CBI has been used for this investigation.

2 CHLORIDE BINDING

2.1 Manufacture and storage of specimens

TABLES 1 and 2 present an analysis of the constituents used.

TABLE 1. Chemical composition of constituents

<u>Material</u>	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O	K ₂ O	Loss of ignition	Specific surface area (m ² /kg)
Slite OPC	62.76	19.74	4.09	2.11	3.3	2.9		1.13	2.11	380
Degerhamn OPC	64.2	21.4	3.57	4.56	0.75	1.89		0.52	1.53	320
Silica fume	0.24	95.73	1.65	0.31	0.08		0.19	1.28		22000
Fly ash (Västerås)	8.8	48.3	26.9	4.4	0.7	1.6		3.8	3.2	

TABLE 2. Mineralogical composition of constituents

Cement	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Slite OPC	59	14	8	6
Degerhamn OPC	59	17	2	15

Specimens of cement paste with the following composition were manufactured:

1. Slite OPC (Ordinary Portland Cement with ~ 8% C₃A), water-cement ration 0.40, 0.50 and 0.60.
2. Degerhamn OPC (Ordinary Portland Cement with ~ 2% C₃A) water-cement ratio 0.40.
3. Slite OPC/10% silica fume, water-cement ratio 0.40.
4. Slite OPC/25% fly ash, water-cement ratio 0.40.
5. Slite OPC/lignosulphonate-based additive, water-cement ratio 0.40.
6. Slite OPC/melamine-based additive, water-cement ratio 0.40.
7. Slite OPC/naphthalene-based additive water-cement ratio 0.40.

In those cases in which chemical additives were used, the dosages applied were in accordance with the manufacturer's instructions. Deionised water was used when casting.

The specimens were cast in teflon moulds with a diameter of 19 mm and a length of 50 mm. To avoid separation all specimens with a water-cement ratio >0.40 and/or with a mineral additive were rotated for about 24 hours after casting. They were then removed from the moulds. During the following 5 days the specimens were stored in a small quantity of deionised water. They were then placed in plastic bags without water. To avoid drying out, the plastic bags were stored in a room with 100% RH.

2.2 Testing

The specimens were about 8 months old when the test was started.

The cement paste was ground in a rotary mill. About 5 g was then weighed and added to 25 ml solution. The composition of the solutions is presented in TABLE 3.

TABLE 3. Chemical composition for solutions in chloride binding test. Cl^- added as NaCl, SO_4^{2-} as K_2SO_4 and OH^- as KOH

Cl^- (mg/l)	SO_4^{2-} /M/	OH^- /M/
3000	0	0
10000	0.02	0.1
20000	0.03	0.5
50000	0.06	2.0
80000	0.2	5.0

Only sample type 1 was tested with all these combinations of solution compositions (125). For other test mixtures, a limited number of solution compositions were selected.

The mixture of ground cement paste and solution was vibrated for 7 days. The sample was then centrifuged and the Cl^- concentration in the solution was determined. The consumption of Cl^- is regarded as bound (chemically bound and physically adsorbed), and can be calculated as a percentage of

the quantity of cement paste. Since the quantity of cement in the weighed cement paste was determined with the aid of loss of ignition, the bound Cl^- can also be calculated as a percentage of the cement weight.

3 RESULTS AND DISCUSSION

Since the number of experimental parameters was extensive, only examples of the results are presented here.

FIG 1 presents the amount of bound chloride for mixture 1 (Slite OPC) as % of the cement weight after the solution was vibrated for 1 week. The initial solution in this case was a chloride solution with 10,000 mg $\text{Cl}^-/1$. As can be seen from the figure, the proportion of bound chloride decreases with increases in the OH^- concentration in the vibrated solution. This interdependency could be noted for all initial solutions. (Cl^- -concentration 3 000 - 80 000 mg/1.)

FIG 2 presents the bound chloride in solutions where, instead of hydroxide, sulphate was added. Here, too, it can be noted that an increase in the SO_4^{2-} -concentration causes a reduction in the Cl^- -binding.

The conclusion to be drawn from this is that the chloride binding depends on the pore solution's concentration of OH^- and SO_4^{2-} . The composition of the pore solution is determined by the composition of the cement and any mineral additives and chemical admixtures which have been used, as well as the composition of solutions which penetrate the concrete from the surface.

A solution of 0.5 M OH^- , 0.03 M SO_4^{2-} and with 3000, 20 000 and 80 000 mg $\text{Cl}^-/1$ respectively was used to investigate the effect of the cement type, mineral additive and chemical admixture. The results are presented in FIG 3.

A comparison of two different OPCs, Slite OPC (8% C_3A) and Degerhamn OPC (2% C_3A), showed that Slite OPC binds less chloride. These results indicate that the chloride binding capacity is dependent on the composition of the cement. It does not seem, however, that it is the cement's C_3A content which is of decisive significance. This conflicts with many references in

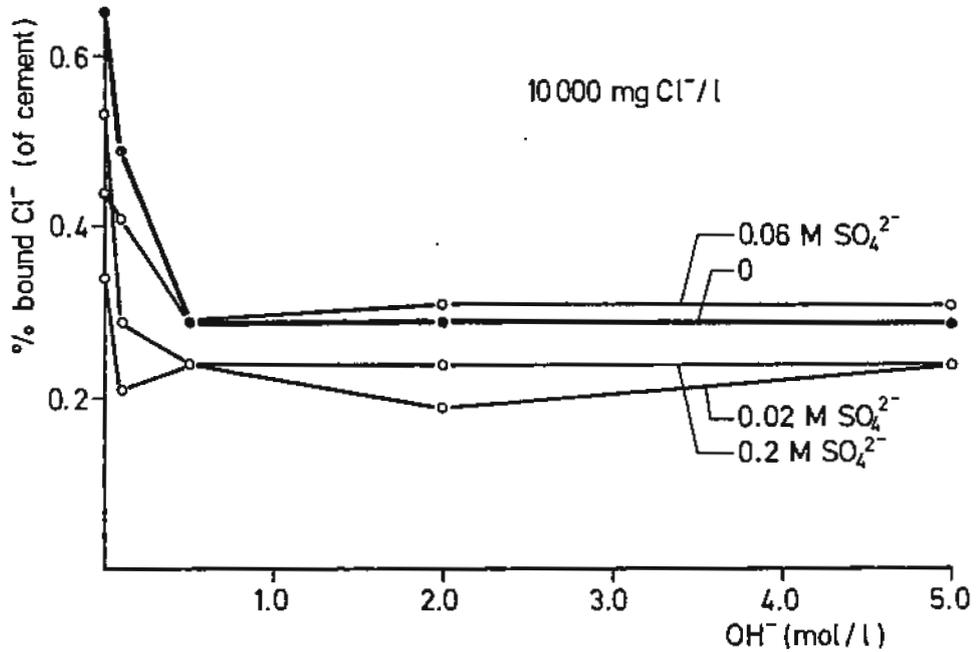


FIG 1. Quantity of bound chloride (calculated as % of cement weight) as a function of the OH⁻-concentration of the initial solution. The chloride concentration of the solution was 10 000 mg Cl⁻/l at the beginning of the experiments.

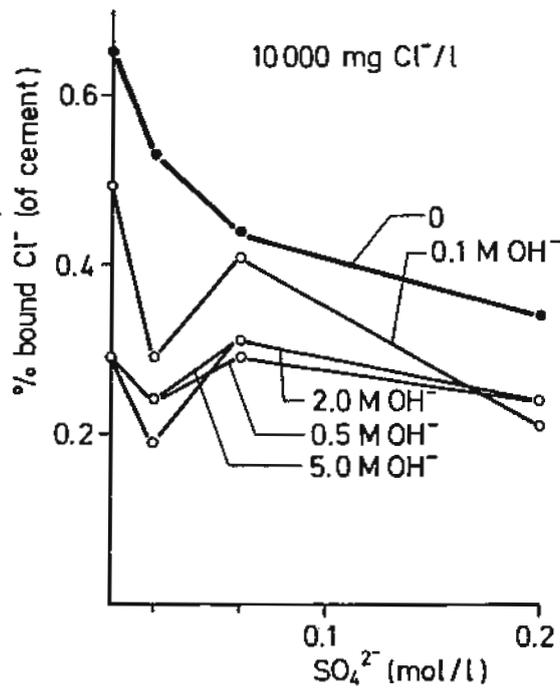


FIG 2. Quantity of bound chloride (calculated as % of the cement weight) as a function of the SO₄²⁻-concentration of the initial solution. The chloride concentration of the solution was 10 000 mg Cl⁻/l at the beginning of the experiments.

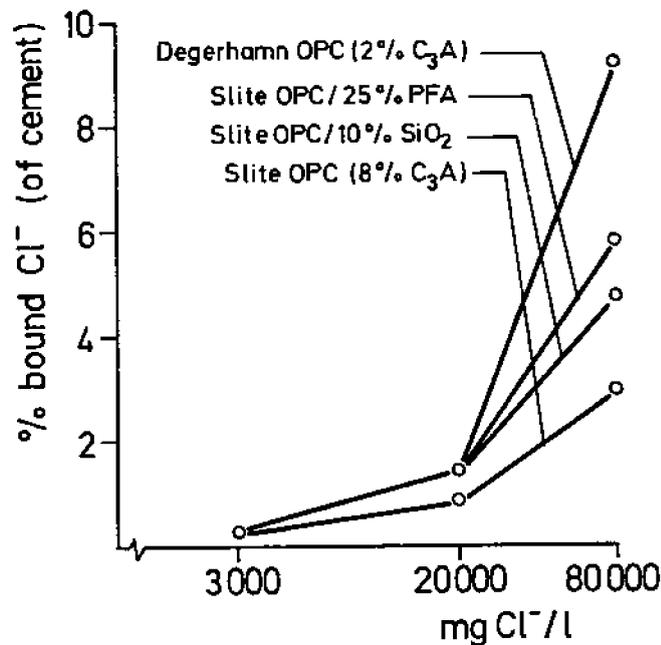


FIG 3. Quantity of bound chloride for mixes with various binder compositions as a function of the Cl⁻-concentration of the initial solution. Initial solution: 0.5 M OH⁻, 0.03 M SO₄²⁻, 3 000, 20 000 and 80 000 mg Cl⁻/l respectively.

the literature, see for example /2/. It could be noted in an investigation carried out by Byfors, Hansson and Tritthart /3/ that the C₃A content was not of decisive significance for the chloride binding. The two factors which, in addition to the C₃A content, essentially distinguish the two cements, Slite OPC and Degerhamn OPC, are the C₄AF content and the alkali content. Degerhamn OPC has a far higher C₄AF content (~15%) compared with Slite OPC (~6%). As a result, the sum of the C₃A and C₄AF contents are higher in Degerhamn OPC (~17%) than in Slite OPC (~14%). This may be one explanation for the higher chloride binding capacity of the Degerhamn cement. Degerhamn OPC is also a low-alkali cement. The measured hydroxide ion concentration in an expressed pore solution amounted to approximately 0.24 M compared with 0.33 M for Slite OPC (samples about 1 year old). Therefore, a second possible explanation for the lower chloride binding capacity of Slite OPC is the high alkalinity.

It is also of interest here to compare the results of chloride binding measured with the aid of the method described in this project, with the results

measured with the aid of the pore solution expression method /3/. The pore solution from a paste sample (Slite OPC) with a water-cement ratio of 0.60, containing 1% Cl^- , proved to have a Cl^- concentration of about 14 000 mg $\text{Cl}^-/1$. A theoretic conversion of this value to bound Cl^- , based on the cement weight, gives approximately 0.4%. This value can be compared with the value measured in the present investigation, 1.2%, for paste with a water-cement ratio of 0.60 vibrated in a solution with an initial concentration of 20 000 mg $\text{Cl}^-/1$, 0.5 M OH^- , 0.03 M SO_4^{2-} . The results from the two methods are thus on the same order of magnitude. The difference may be due to errors which arose in connection with the assumptions in the conversion and to the fact that the vibrated solution in the present investigation did not have the same composition as the pore solution. Another difference is that the present results are for hardened paste exposed to Cl^- whereas the pore solution data are for Cl^- cast into the samples. The ground paste can also have a higher chloride binding capacity due to its greater specific surface.

FIG 3 also shows that an addition of 10% silica fume to Slite OPC increased its chloride binding capacity. Similar results were noted in a parallel investigation, see /3/. It is also known that the silica fume reacts with the cement alkali so that the pore solution receives a lower OH^- -concentration. The increased chloride binding in this case may thus be due to a low OH^- -concentration in the pore solution. Another likely explanation is that the specific surface of the binder increases when silica fume is added. It should be noted here that Page and Vennesland have shown that the chloride binding was reduced when silica fume was added /5/. No explanation has yet been found for these conflicting results.

An addition of 25% fly ash also proved to increase the chloride binding. Other investigations have shown that fly ash does not affect the chloride binding to any noteworthy extent, see for example /3/, or that the chloride binding tends to increase /3/, /4/. The differences in results here may be due to differences in the composition and properties of the fly ashes and again the effect of Cl^- cast in versus exposure of hardened paste to Cl^- .

As can be seen in FIG 3, the proportion of bound chloride (based on the cement weight) increases when the chloride concentration of the solution increases. It is thus a question of chemical and physical equilibrium between free and bound ions throughout the entire process.

FIG 4 presents the chloride binding for paste manufactured of Ordinary Portland Cement (Slite OPC) with a plasticizer. All chemical admixtures, based on melamine, lignosulphonate and naphthalene respectively increased the chloride binding capacity. A possible explanation is that the admixtures give good dispersion and a high specific surface area. It is, however, difficult to discuss the results in detail since we know nothing of how these agents affect the composition of the pore solution.

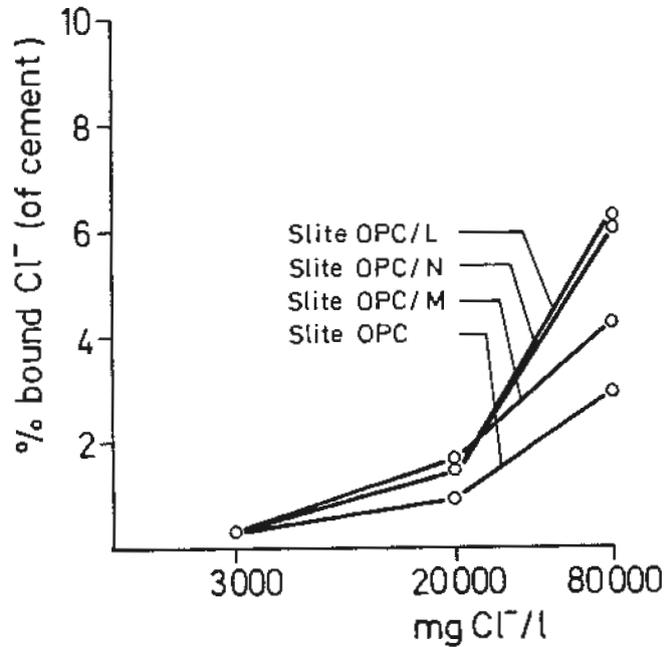


FIG 4. Quantity of bound chloride for mixes with various chemical admixtures as a function of the Cl⁻-concentration of the initial solution.
N = naphthalene, L = lignosulphonate, M = melamine.
Initial solution: 0.5 M OH⁻, 0.03 M SO₄²⁻, 3 000, 20 000 and 30 000 mg Cl⁻/l respectively.

4 CONCLUSION

The results from this investigation show that the chloride binding capacity of the cement paste is influenced by the pore solution's concentration of Cl⁻, OH⁻ and SO₄²⁻. The chemical composition of the pore solution is, in turn, dependent on the composition of the cement and on the influence of the external environment (penetrating solutions, carbonation etc).

It is highly probable that the specific surface of the binder and, where applicable, the sum of the C_3A and C_4AF contents are also significant for the chloride binding capacity. This can also be seen in a parallel investigation /4/.

Another factor which affects chloride binding capacity is the salt cation, see /6/, /7/, /8/.

Since mineral additives and chemical admixtures influence both the composition of the pore solution and the mineralogical composition and specific surface of the binder, it is also natural that the chloride binding capacity is changed when these agents are used. The results from the present investigation show that adding silica fume or fly ash to the cement increases its chloride binding capacity. This result applies, however, to the specific materials used in the investigation. Since various mineral additives, particularly fly ash, can vary considerably in composition and fineness, it is also likely that their influence on the chloride binding capacity can vary.

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