

International Congress on Durability of Concrete

Resistance of concrete against combined attack of chlorides and sulphates

--Manuscript Draft--

Manuscript Number:	ICDC2012-D-11-00042R1
Full Title:	Resistance of concrete against combined attack of chlorides and sulphates
Article Type:	Full Draft Paper - Submitted For Review
Section/Category:	Concrete deterioration mechanisms
Keywords:	Chlorides; Sulphates; Temperature; Combined attack; C3A; Chloride binding
Corresponding Author:	Mathias Maes Magnel Laboratory for Concrete Research, Ghent University Ghent, BELGIUM
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Magnel Laboratory for Concrete Research, Ghent University
Corresponding Author's Secondary Institution:	
First Author:	Mathias Maes
First Author Secondary Information:	
All Authors:	Mathias Maes Elke Gruyaert Nele De Belie
All Authors Secondary Information:	
Manuscript Region of Origin:	BELGIUM
Abstract:	<p>A lot of damage is reported for constructions in marine environments, due to the aggressiveness of sea water containing chlorides and sulphates. Chlorides affect durability by initiating corrosion of the reinforcement steel, and sulphates by deteriorating the concrete through formation of expansive reaction products. This research compares single-ion attack and combined attack. Combined attack simulates concrete deterioration in marine environments more realistically. However, several factors influence concrete resistance against chlorides and sulphates: cement type and C3A-content, additions, age, temperature, etc. To examine these influences concrete mixtures containing ordinary Portland cement, high sulphate resistant cement, or blast furnace slag as 50 % and 70 % cement replacement were compared. Resistance against chlorides and chlorides combined with sulphates was tested by natural diffusion tests based on NT Build 443. Specimens were tested at varying ages since chloride penetration decreases with concrete age. The first test series was performed at three different temperatures namely 5 °C, 12.5 °C and 20 °C to quantify to which extent lower exposure temperatures slow down diffusion rates. It is clear that diffusion coefficients and colour change boundaries decrease when temperatures lower. Next, the influence of sulphates on the chloride penetration was examined. The results show that, when 55 g/l Na₂SO₄ was added to a 165 g/l NaCl solution, the colour change boundaries and diffusion coefficients increase for ordinary Portland cement concrete and 50 % slag concrete, but not for HSR concrete. However, for all concretes chloride binding decreases when sulphate content increases. Generally the C3A-content of the cement plays a major role in the attack mechanism and in the binding behaviour of chlorides and sulphates. So, when both ions penetrate together, C3A influences this multi-ion transport as well as the concrete durability.</p>

RESISTANCE OF CONCRETE AGAINST COMBINED ATTACK OF CHLORIDES AND SULPHATES

Mathias Maes¹, Elke Gruyaert¹ and Nele De Belie¹

¹Magnel Laboratory for Concrete Research, Ghent University,
Technologiepark-Zwijnaarde 904, 9052 Ghent, Belgium
E-mail: nele.debelie@ugent.be

ABSTRACT

A lot of damage is reported for constructions in marine environments, due to the aggressiveness of sea water containing chlorides and sulphates. Chlorides affect durability by initiating corrosion of the reinforcement steel, and sulphates by deteriorating the concrete through formation of expansive reaction products. This research compares single-ion attack and combined attack. Combined attack simulates concrete deterioration in marine environments more realistically. However, several factors influence concrete resistance against chlorides and sulphates: cement type and C₃A-content, additions, age, temperature, etc. To examine these influences concrete mixtures containing ordinary Portland cement, high sulphate resistant cement, or blast furnace slag as 50 % and 70 % cement replacement were compared. Resistance against chlorides and chlorides combined with sulphates was tested by natural diffusion tests based on NT Build 443. Specimens were tested at varying ages since chloride penetration decreases with concrete age. The first test series was performed at three different temperatures namely 5 °C, 12.5 °C and 20 °C to quantify to which extent lower exposure temperatures slow down diffusion rates. It is clear that diffusion coefficients and colour change boundaries decrease when temperatures lower. Next, the influence of sulphates on the chloride penetration was examined. The results show that, when 55 g/l Na₂SO₄ was added to a 165 g/l NaCl solution, the colour change boundaries and diffusion coefficients increase for ordinary Portland cement concrete and 50 % slag concrete, but not for HSR concrete. However, for all concretes chloride binding decreases when sulphate content increases. Generally the C₃A-content of the cement plays a major role in the attack mechanism and in the binding behaviour of chlorides and sulphates. So, when both ions penetrate together, C₃A influences this multi-ion transport as well as the concrete durability.

Key-words: Chlorides, Sulphates, Temperature, Combined attack, C₃A, Chloride binding.

INTRODUCTION

A lot of damage is reported for constructions in marine environments. Marine environments are very aggressive, since sea water consists mainly of chlorides and sulphates. Chlorides affect durability by initiating corrosion of the reinforcement steel, and sulphates by deteriorating the concrete itself.

The major fraction of sea water consists of chlorides. There are different ways in which chlorides can penetrate into the concrete: diffusion when the concrete is saturated, capillary sorption when the surface is dehydrated or when the concrete is cracked, electrical migration, thermal migration or under the influence of a hydrostatic gradient [1, 2]. In this research, an accelerated test method was applied, namely an accelerated natural diffusion test by increasing the chloride concentration of the test solution. Diffusion of Cl⁻ ions is described by Fick's laws. Fick's first law (Eq. 1) counts for steady-state conditions, which means there is no change in concentration with time.

$$J = -D \frac{dc}{dx} \quad (1)$$

Fick's second law (Eq. 2) counts for non-steady-state conditions, meaning that chloride concentration will change in time. However, the diffusion coefficient is assumed to be constant.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

Here J is the flux (mol/m²s), D is the diffusion coefficient (m²/s), x the depth (m), t the time (s) and c the concentration (mol/m³).

Solving the second law (Eq. 2) using the boundary conditions $c = c_0$ ($x = 0, t > 0$) and $c = 0$ ($x > 0, t = 0$), results in the classical error function solution (Eq. 3).

$$c(x, t) = c_0 \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (3)$$

Diffusion is not only time-dependant but also temperature-dependant. Nevertheless, most of the laboratory tests are performed at 20°C. According to several researchers [3 - 5], the diffusion coefficient of concrete will increase when the temperature increases. These researchers investigate temperatures ranging from 20°C until 105°C. Since the temperatures in marine environments in Western Europe are mainly in the range of 5°C – 20°C the natural diffusion tests in this research were conducted at 5°C, 12.5°C and 20°C.

It is important to notice that corrosion will only be initiated by the free chlorides and not by the fraction that is chemically bound to the cement hydrates or physically adsorbed at the pore walls. Chloride binding is a significant factor related to reinforced concrete durability for three reasons [6]: reduction of the free chloride concentration in the vicinity of the reinforcing steel will reduce the risk of corrosion; chloride binding will delay the chloride penetration; formation of Friedel's salt results in a less porous structure and slows down the transport of Cl⁻ ions. Friedel's salt (3CaO·Al₂O₃·CaCl₂·10H₂O) is the result of chemical binding between chlorides and C₃A. Chemical binding can also occur between chlorides and C₄AF. Besides, physical binding occurs due to interaction with CSH.

Next to chlorides, sulphates are also a main compound of sea water. Sulphate attack can be divided in two groups: external and internal attack. In this research, only the first group is examined. External sulphate attack occurs when water contaminated with sulphates penetrates into the concrete. These ions penetrate into the concrete by means of diffusion or capillary suction. Sulphates are mostly found in the form of sodium sulphate or magnesium sulphate, Na_2SO_4 and MgSO_4 , respectively. In current paper, only the influence of Na_2SO_4 is examined. The factors influencing the rate of external attack are: the quantity of sulphate ions, the possibility of the sulphates to penetrate into the concrete and the volume of C_3A in the cement and the type of cement used to make the concrete.

Sulphates react with the lime formed during the hydration process of the Portland clinker. One of the reaction products is calcium sulphate or secondary gypsum. This calcium sulphate only reacts with hydrated calcium aluminates, C_3A , and forms ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$). Ettringite has the ability to swell strongly, which results in internal stresses that lead to cracking and destruction of the concrete.

At low temperatures and in presence of soluble carbonate and reactive silicate, thaumasite ($\text{Ca}_3\text{Si}(\text{CO}_3)(\text{SO}_4)(\text{OH})_6\cdot12\text{H}_2\text{O}$) is formed. This is not expansive but lowers the strength and has a negative influence on the microstructure. Thaumasite is considered as a reaction product of sulphate attack which is formed in later stages of the attack process. According to Glasser [6] and Brown et al. [7], the formation of thaumasite is always preceded by the formation of ettringite. It is generally assumed that thaumasite is only formed at temperatures below $15\text{ }^\circ\text{C}$. However, some researchers also found thaumasite at temperatures higher than $15\text{ }^\circ\text{C}$ [8-10]. In the current paper, the influence of the temperature on the sulphate attack mechanism was not examined yet.

Generally the C_3A -content of the cement plays a major role in the attack mechanism of sulphates and in the binding behaviour of chlorides. When both ions penetrate the concrete together, C_3A definitely influences this multi-ion transport as well as concrete durability.

In this research, the influence of the multi-ion transport on the proper attack mechanisms was examined next to the influence of the temperature on chloride penetration. Accelerated tests were conducted in the laboratory. These tests are natural diffusion tests where after colour change boundaries and diffusion coefficients are calculated. In the end, the influence of sulphates on the chloride attack mechanism should become clear, as well as the influence of the temperature.

MATERIALS AND METHODS

Concrete mixtures

To determine the resistance to chlorides, four different concrete mixtures were prepared (Table 1): two Portland cement mixtures and two blast furnace slag (BFS) mixtures. The Ordinary Portland Cement mixture (OPC) was seen as the reference mixture. The other Portland cement mixture contained High Sulphate Resistant cement (HSR). The two BFS concrete mixtures contained high amounts of slag. The cement replacement levels amounted to 50 % (S50) and 70 % (S70), respectively. The total binder content (cement + slag) was maintained at 350 kg/m^3 and the water-to-binder factor (W/B) at 0.45. This is in accordance with EN 206-1 [11],

when the concrete is applied in an ES3 environment. Superplasticizer (SP) was added to the mixture to obtain a slump between 100 mm – 150 mm (consistency class S3).

Table 1 - Concrete mixtures

	OPC	HSR	S50	S70
Sand 0/4 (kg/m ³)	781	781	781	781
Aggregate. 2/8 (kg/m ³)	619	619	619	619
Aggregate 8/16 (kg/m ³)	480	480	480	480
CEM I 52.5 N (kg/m ³)	350	-	175	105
CEM I 52.5 N HSR (kg/m ³)	-	350	-	-
Slag (kg/m ³)	-	-	175	245
Water (kg/m ³)	157.5	157.5	157.5	157.5
W/B (-)	0.45	0.45	0.45	0.45
S/B (%)	0	0	50	70
SP (ml/kg B)	1.2	1.2	2.9	2.9
Slump	S3	S3	S3	S3
Strength class	C45/55	C45/55	C35/45	C30/37

In Table 2 the chemical composition of the different cement types and the slag is given, determined in accordance with EN 196-2 [12] and using Wavelength Dispersive X-ray Spectroscopy (WD-XRF). Since HSR cement is used because of its low C₃A-content, the C₃A-content was calculated by using the Bogue equations. According to EN 197-1 [13], the C₃A-content for HSR cement is limited to 3 %. In current research, the C₃A-content for HSR amounts to 2.50 % and corresponds to the standard. For OPC the C₃A-content is 7.92 %.

Table 2 – Chemical composition of the cement and slag

Content [%]	OPC	HSR	BFS
CaO	63.37	63.90	41.24
SiO ₂	18.90	21.62	36.37
Al ₂ O ₃	5.74	3.53	9.83
Fe ₂ O ₃	4.31	4.05	0.26
SO ₃	3.34	2.40	1.62
MgO	0.89	1.82	7.41
K ₂ O	0.73	0.51	0.41
CO ₂	0.50	0.34	0.90
Na ₂ O	0.47	0.15	0.28
Cl-	-	0.026	0.02
Sulphide content	-	0.05	0.79
Insoluble residu	0.41	0.48	0.43
Loss on ignition	1.51	0.95	1.30

Curing and sample preparation

For each mixture, the total mixing time was 3 minutes. Firstly sand, aggregates, cement (and slag) were mixed dry for 1 minute, after which water and SP were added and mixing continued

for 2 minutes. The characteristics of the fresh concrete are also tabulated in Table 1. The slump was measured according to EN 12350-2 [14] with indication of the consistency class.

Cubes with a 150 mm side were casted and cured at 20 °C and a relative humidity (R.H.) higher than 95 %. Demoulding took place the next day whereupon the specimens were stored again under the same conditions until the age of 14 days, except for the 70 % slag mixture. Those cubes were demoulded after 2 days because of the slower hardening. At the age of 14 days, a core with a diameter of 100 mm was drilled out of each cube. This cylinder was cut in three specimens with a thickness of 50 mm. These specimens were stored again until the age of testing, namely 28 days or 84 days.

Diffusion test

Preparation

The resistance to chloride penetration was evaluated experimentally using the natural diffusion test as described in NT Build 443 [15]. This method is based on Fick's second law (Eq. 2). First, the specimens were saturated in a 4 g/l $\text{Ca}(\text{OH})_2$ solution. After 10 days of immersion in this solution, the specimens were coated, except for the casting surface. However, NT Build 443 prescribes to remove the outermost 10 mm of the casting surface; this was not performed in this research. The coated specimens were placed in the 4 g/l $\text{Ca}(\text{OH})_2$ solution for another 10 days because then the specimens reached a constant mass. Afterwards the specimens were placed in the test solution. The composition of the test solution and the test temperature depended on the characteristic under investigation.

Temperature

To determine the influence of the storage temperature, an aqueous NaCl solution with a concentration of 165 g NaCl per l solution was used, as described in NT Build 443 [15]. For each concrete mixture the specimens were placed in this solution at three different temperatures. Since the temperatures in marine environments in Western Europe are mainly lower than 20 °C, the test temperatures amounted to 20 °C, 12.5 °C and 5 °C.

Sulphate content

Since the influence of the sulphate content on the chloride attack mechanism was investigated, three different test solutions were used for this purpose. The first solution was the reference solution, namely a 165 g/l NaCl solution in accordance with NT Build 443 [15]. The other solutions contained a certain sulphate content on top of the 165 g/l NaCl. The sulphate content amounted to 27.5 g/l Na_2SO_4 and 55 g/l Na_2SO_4 , respectively. The temperature during the immersion time was maintained at 20 °C.

Measurement

After 7 weeks storage in the test solution, the chloride penetration was measured by means of potentiometric titrations and by measuring the colour change boundary.

The colour change boundary was determined by spraying a 0.1 M AgNO_3 solution onto both halves of a split specimen, which results in a visible white deposit of AgCl_2 where free chlorides have penetrated into the concrete. At least three samples were split for every measurement (per concrete type and per solution and temperature). For each half specimen the penetration depth

was measured, with an accuracy of 1 mm, at 6-9 places with an interval of 10 mm. When the penetration front was blocked by aggregates, the measurement was moved to the nearest point on the front without significant blocking.

To obtain a chloride profile, chloride concentrations have to be measured at different depths. Therefore potentiometric titrations were performed. A Metrohm MET 702 automatic titrator was used for this purpose. Powder was collected from the cylindrical specimens up to a depth of 20 mm, using a profile grinder. Layers of 2 mm thickness were ground. For the reference mixture, the HSR mixture and S50 mixture tested in a 165 g/l NaCl solution at 20 °C, three specimens were subjected to his method, while for all the other test configurations only one specimen was used. The extraction of chlorides from the powder was based on the method described by Yuan [16]. Water-soluble chlorides were extracted in water, while the total chloride content was determined by acid-extraction. The water-soluble chloride concentration gives an indication of the free chloride content in the concrete. In this research, the free chloride content was assumed to be 80 % of the water-soluble chloride content, in accordance with the findings of Yuan [16]. Next, a potentiometric titration, with 0.01 mol/l AgNO₃-solution was performed. Chloride contents were calculated using Eq. 4 and 5 (c_t = total chloride content, c_w = water-soluble chloride content).

$$c_t (\%) = \frac{10 \times 100 \times 35.45 \times 0.01 \times \text{Vol. AgNO}_3 \text{ (ml)}}{1000 \times 2} \quad (4)$$

$$c_w (\%) = \frac{10 \times 100 \times 35.45 \times 0.01 \times \text{Vol. AgNO}_3 \text{ (ml)}}{1000 \times 2.5} \quad (5)$$

Where 10 represents the dilution factor; 35.45 is the atomic mass of chlorides (g/mol); 0.01 is the concentration of the titration solution (mol/l); and 2 (or 2.5 for water-soluble chloride content) is the mass of the concrete powder in the extraction solution. 0.01 mol/l can be replaced by the exact concentration of the AgNO₃-solution, resulting from the calibration.

Since the water extraction method is influenced by many factors [17] (e.g. water to solid ratio, temperature, size of particles, etc.), repeatability was checked. Triplicate tests were conducted on a homogenized sample. The results indicate that the water extraction method is quite repeatable, since the coefficient of variation ranged from 0.7 % to 4.8 %. This corresponds to the repeatability results obtained by Yuan [16].

Non-steady-state diffusion coefficients were obtained from the measured chloride profiles, in accordance to the method described in NT Build 443 [15]. The surface concentration and non-steady-state diffusion coefficient were calculated by adapting Eq. 6 to the measured chloride profiles by applying a non-linear regression analysis in accordance with the least squares method.

$$c_t(x, t) = c_s - (c_s - c_i) \operatorname{erf}\left(\frac{x}{\sqrt{4D_{nssd}t}}\right) \quad (6)$$

Where $c_t(x, t)$ is the chloride concentration at depth x and time t (mass % concrete), c_i the initial chloride concentration (mass % concrete), c_s the chloride concentration at the surface (mass % concrete), D_{nssd} the non-steady-state diffusion coefficient (m²/s), x the distance from the surface until the middle of the considered layer (m) and t the exposure time (s).

Compared to the mass of concrete, it was reasonable to assume that the initial chloride concentration c_i in Eq. 6 equaled 0 %. The first layer was excluded from the regression analysis, since the measured chloride concentration in the first layer was not always as accurate. According to NT Build 443 [15], this calculation procedure should be applied to the total chloride profile. However, in this research, the error function (Eq. 6) was fitted to the free chloride profile.

RESULTS

Chloride attack – influence of the temperature

Colour change boundary

Figure 1 shows the average colour change boundaries (ccb's) and the standard deviations on the individual values for the different concrete mixtures stored for 7 weeks in a 165 g/l NaCl solution at 20 °C, 12.5 °C and 5 °C. The test preparation (saturation and coating) started at 28 days on the one hand, and at 84 days on the other hand.

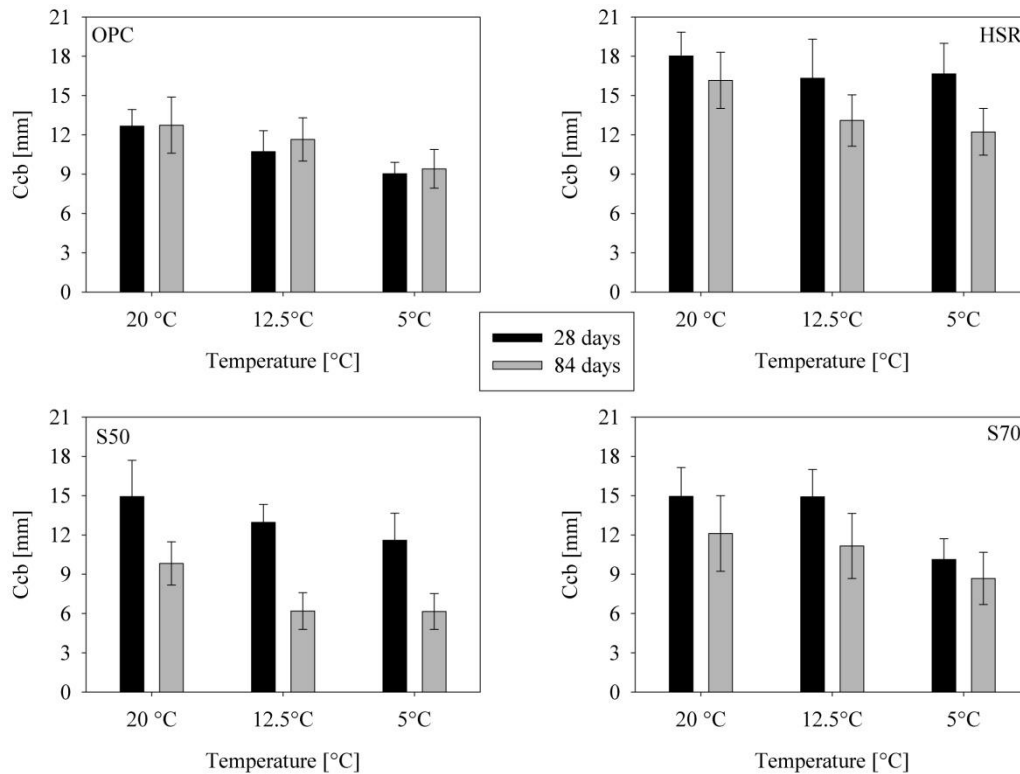


Figure 1 - Colour change boundaries for OPC, HSR, S50 and S70 concrete with an age of 28 and 84 days at the start of the test stored in a 165 g/l NaCl solution at 20 °C, 12.5 °C and 5 °C for 7 weeks.

From these graphs it is clear that the ccb decreases when the temperature decreases, regardless the concrete composition and the concrete age. A statistical one-way ANOVA with a Dunnett T3 Post Hoc test (level of significance = 0.05) indicates that the decrease in temperature from 20 °C to 5 °C as well as the decrease from 20 °C to 12.5 °C and from 12.5 °C to 5 °C result in a significant decrease in chloride penetration depth.

Looking more in detail, it becomes clear that the highest ccb's were measured for HSR at 28 days as well as at 84 days. Since the C_3A -content of this mixture is much lower compared to OPC, less chlorides will chemically bind and free chlorides can penetrate deeper into the concrete. The lowest values at a starting age of 28 days were measured for OPC. Although at a starting age of 84 days the ccb's for S50 were lower. Besides, S50 showed the biggest decrease as a function of the concrete age. This is probably due to the high slag content. The latent hydraulic characteristics of the slag make the hydration reaction occurs slower than for Portland cement. This means that slag concrete will have a denser microstructure at later age, which makes it more difficult for the chlorides to penetrate into the concrete. For the same reason, the ccb's for S70 decrease as well, although it could be that because of the high slag content, these values will decrease further. The temperature will have an influence on the hydration process as well. This will be investigated more in detail in further research. Considering this, it is clear that the slag concrete mixture with 50 % cement replacement shows the best resistance to chloride penetration, especially at low temperatures.

Diffusion coefficient

Figure 2 gives the free chloride profiles, measured after 7 weeks storage in a 165 g/l NaCl solution at 20 °C, 12.5 °C and 5 °C. The test preparation (saturation and coating) started at the age of 28 days. For OPC, HSR and S50 it is clear that the chloride profile obtained after immersion in a chloride solution at 5°C shows the lowest values for the chloride concentrations at a certain depth. In general, increasing slag contents result in more steep chloride profiles.

To compare the influences of the temperature on the chloride penetration in a better way, the chloride diffusion coefficients were calculated by fitting these chloride profiles, using a non-linear regression analysis. These results are shown in Figure 3. From these results it can be seen that, generally, the non steady-state diffusion coefficient decreases when the temperature decreases from 20 °C to 5 °C. However, the decreasing trend is not as clear as it was for the colour change boundaries. Especially for the slag concrete mixtures, temperatures decreasing from 20 °C to 12.5 °C or from 12.5 °C to 5 °C do not provide a drop in diffusion coefficients. In contrast with the findings based on measuring the ccb at 28 days age, the lowest diffusion coefficients were obtained for S70 and S50 concrete. In accordance with previous measurements in this research, the highest values were obtained for HSR concrete.

It should be remembered that only one specimen of each mixture was tested yet, except for OPC, HSR and S50 at 20 °C. So it was not possible to do a profound statistical analysis. However, looking at the graph it seems there is interaction between the mixture and the temperature since none of the curves are parallel. This means that the effect of the temperature on the chloride resistance depends on the type of concrete mixture. It is clear that the temperature influence is bigger for the Portland cement mixtures than for the slag mixtures, since the differences in diffusion coefficients are smaller. In general, the diffusion coefficients of slag concrete, S50 and S70, are much lower than these of OPC and HSR. Further research (e.g. tests at later ages) is needed to show the influence of the temperature on the diffusion coefficient more in detail.

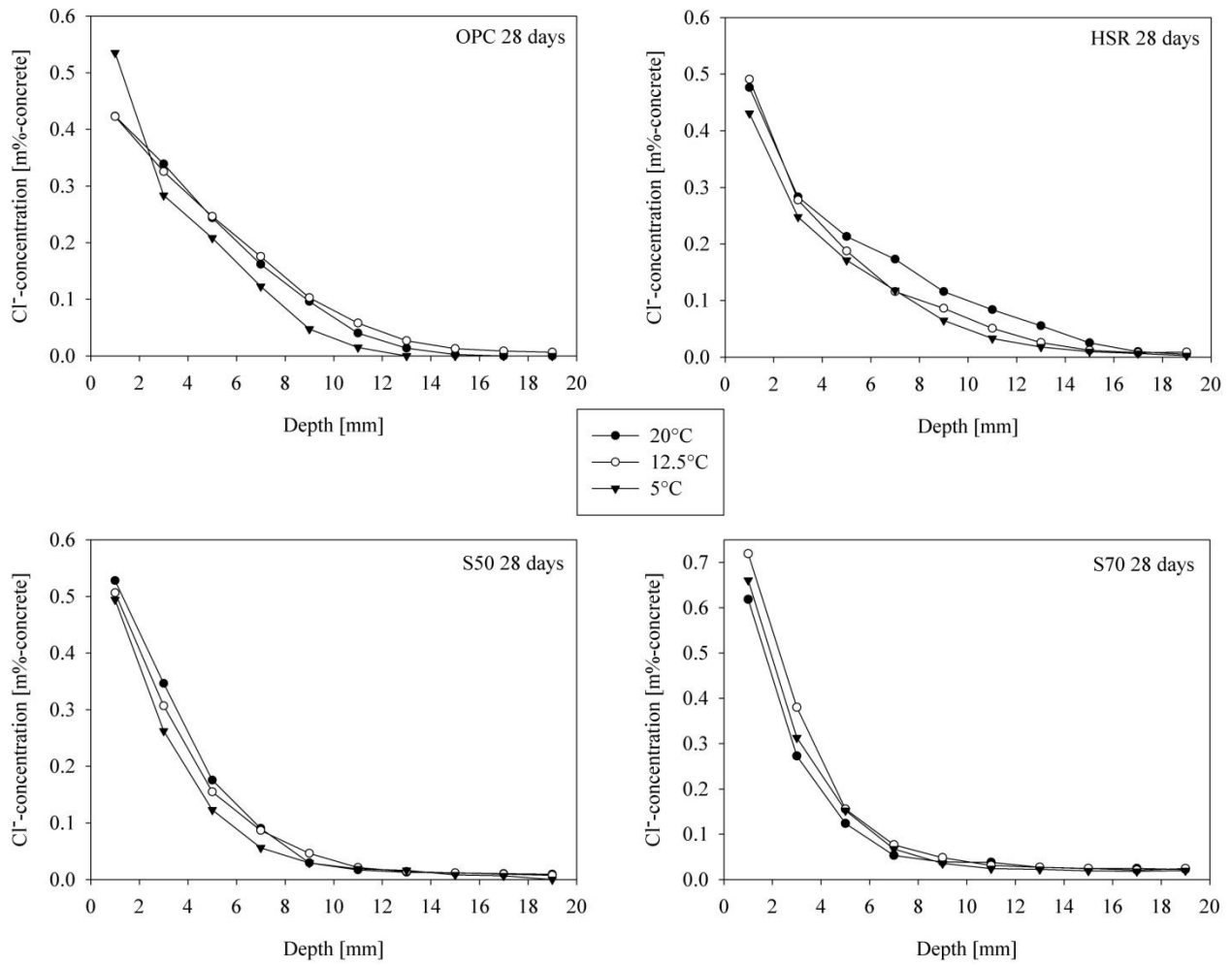


Figure 2 - Free chloride profiles for OPC, HSR, S50 and S70 obtained after 7 weeks immersion in a 165 g/l NaCl solution at 20°C, 12.5°C or 5 °C.

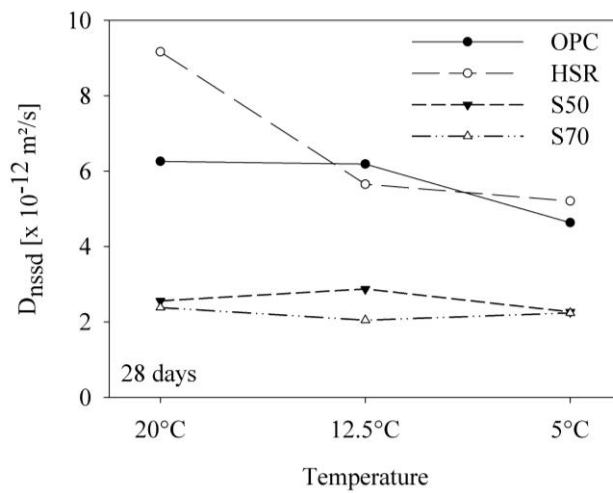


Figure 3 - Diffusion coefficients for OPC, HSR, S50 and S70 concrete with an age of 28 days at the start of the test stored in a 165 g/l NaCl solution at 20 °C, 12.5 °C and 5 °C for 7 weeks.

Chloride attack – influence of the sulphate content

Colour change boundary

Figure 3 shows the average ccb's with the standard deviations on the individual values, measured after 7 weeks immersion in a 165 g/l NaCl solution, a 165 g/l NaCl + 27.5 g/l Na₂SO₄ solution or a 165 g/l NaCl + 55 g/l Na₂SO₄ solution. OPC, HSR and S50 concrete were tested at an age of 28 days.

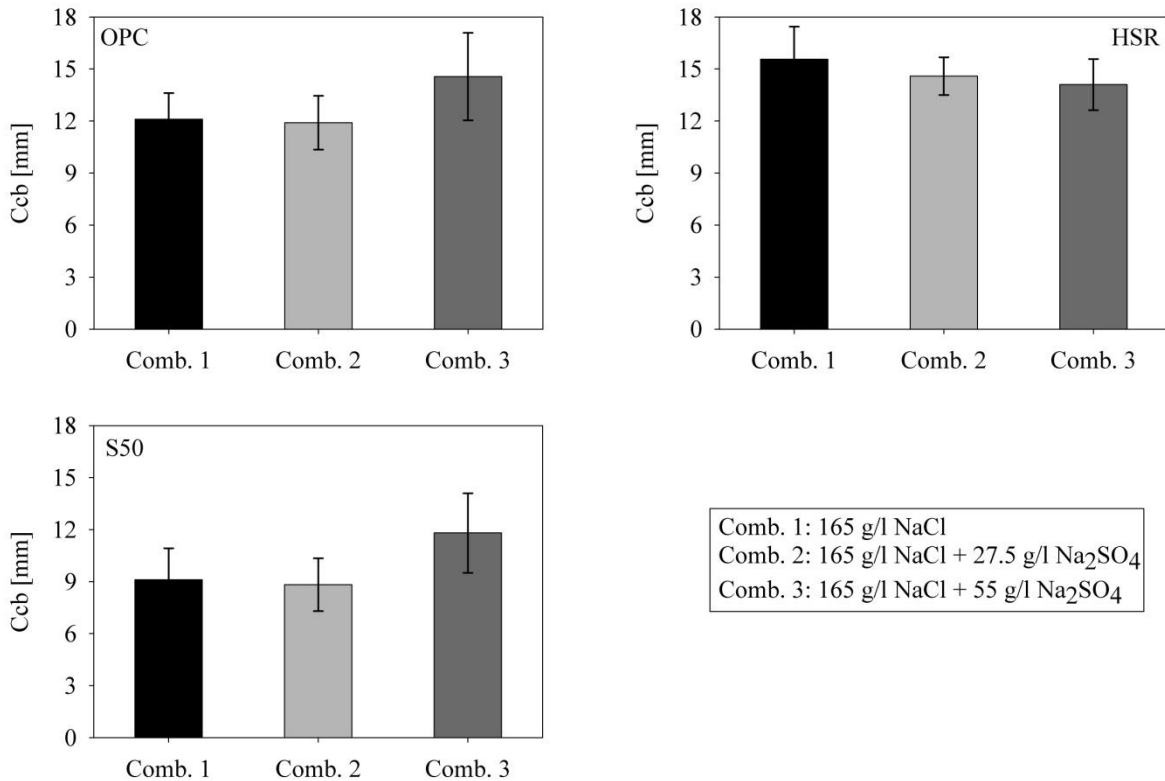


Figure 4 - Colour change boundaries for OPC, HSR and S50 concrete, with an age of 28 days at the start of the test, stored in combined chloride and sulphate solutions at 20 °C for 7 weeks.

It is clear that there is a difference in ccb for specimen immersed in comb. 1 compared to the ccb's for specimen immersed in comb. 3. According to a one-way ANOVA with a Dunnett T3 Post Hoc test (level of significance = 0.05) the measured ccb's after storage in comb.1 and comb.2 are only significantly different from the ccb's obtained after storage in comb.3. However, since there is interaction between the mixture and the sulphate content, the influence is different for different mixtures. A more detailed analysis shows that an increasing sulphate content results in an increase in ccb for OPC and S50, while the opposite can be mentioned for HSR concrete. These particular differences are significant when the sulphate content amounts to 55 g/l. Based on these results it can be determined that a sulphate content of 27.5 g/l Na₂SO₄ added to a 165 g/l NaCl solution has no influence on the chloride penetration depth. So a sulphate content of 55 g/l Na₂SO₄ influences the chloride penetration depth certainly.

Diffusion coefficient

Table 3 gives the diffusion coefficients obtained from fitting the free chloride profiles, measured after 7 weeks storage in a 165 g/l NaCl solution, a 165 g/l NaCl + 27.5 g/l Na₂SO₄ solution or a 165 g/l NaCl + 55 g/l Na₂SO₄ solution at 20 °C. The test preparation (saturation and coating) started at the age of 28 days.

Table 3 - Diffusion coefficients for OPC, HSR, S50 and S70 concrete, with an age of 28 days at the start of the test, after 7 weeks storage in a 165 g/l NaCl solution (Comb. 1), a 165 g/l NaCl + 27.5 g/l Na₂SO₄ solution (Comb. 2) or a 165 g/l NaCl + 55 g/l Na₂SO₄ solution (Comb. 3) at 20 °C.

	D_{nssd} [10⁻¹² m²/s]		
	Comb. 1	Comb. 2	Comb. 3
OPC	6.257	6.057	8.016
HSR	9.268	8.841	8.821
S50	2.604	3.704	2.501

The diffusion coefficients of OPC, obtained after storage in combined solutions, show an increase when the sulphate content increases above 27.5 g/l. Adding 27.5 g/l Na₂SO₄ or less to a 165 g/l NaCl solution has no obvious influence. These results are comparable to the results obtained from measuring the ccb. Also for HSR, the diffusion coefficients show a similar trend as the ccb. Here, the diffusion coefficients stay quite equal, even after storage in the chloride solution diluted with the biggest sulphate content. This phenomenon can be explained by the C₃A-content of the cement. Chlorides as well as sulphates react with the C₃A to form Friedel's salt and ettringite, respectively. The more chlorides can bind, the lower the ccb and D_{nssd}. This means, when sulphates are added to the solution, less C₃A is left for the chlorides to bind. This results in an increase in ccb and D_{nssd}. Except for the HSR mixture, since HSR cement has a low C₃A-content from the beginning. So the binding possibilities for chlorides are already very low, and adding sulphates to the solution does not have a big influence on the chloride binding.

Based on the diffusion coefficients for S50, it was not possible yet to see some kind of a trend. This is in contrast with the results obtained from the ccb. There it was clear that a sulphate content of 55 g/l added to the chloride solution results in an increase of the chloride penetration. Based on the diffusion coefficients this trend was not found.

Chloride binding

The difference between the total chloride content and free chloride content in the chloride profiles, gives an indication of the bound chloride content. The binding capacity can also be plotted as binding isotherms. Figure 5 shows the bound chloride content in function of the free chloride content using a Freundlich binding isotherm (Eq. 7).

$$c_b = \alpha c^\beta \quad (7)$$

Where α and β are empirical constants, c_b bound chloride content (mg/g binder) and c free chloride content (mol/l).

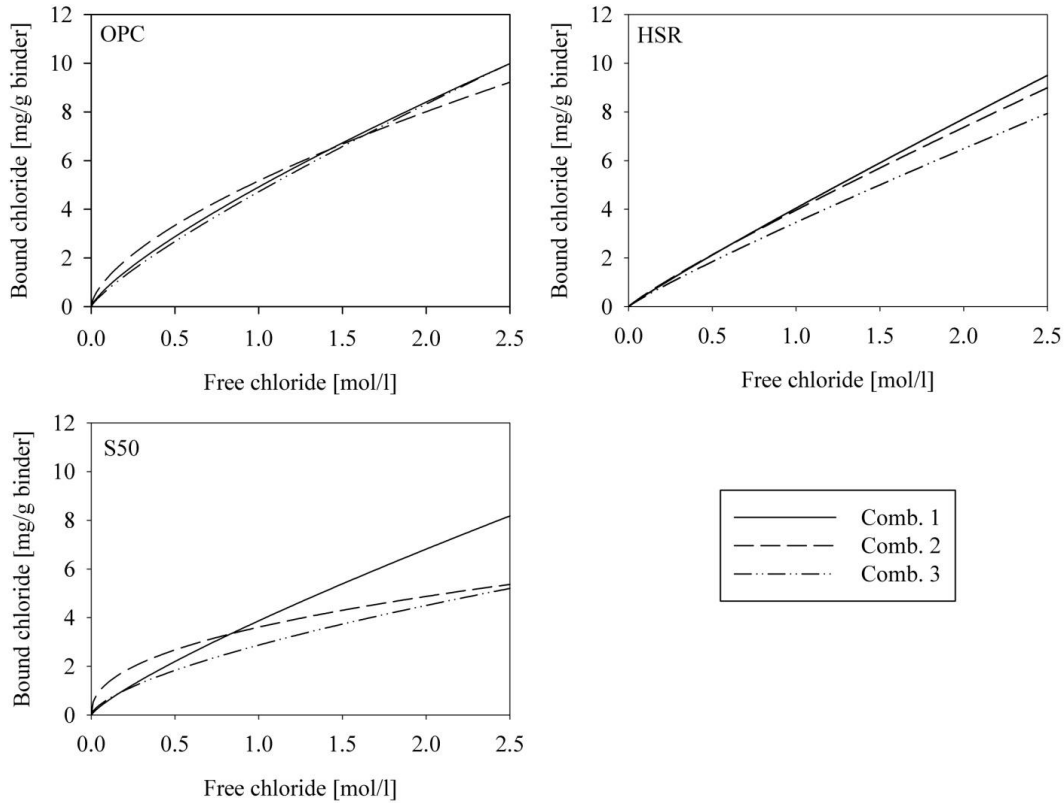


Figure 5 - Freundlich binding isotherms for OPC, HSR and S50 concrete after 7 weeks storage in a 165 g/l NaCl solution (Comb. 1), a 165 g/l NaCl + 27.5 g/l Na₂SO₄ solution (Comb. 2) or a 165 g/l NaCl + 55 g/l Na₂SO₄ solution (Comb. 3) at 20 °C.

The regression parameters are summarized in Table 4. As can be seen, R² shows values above 0.900 for all mixtures except for S50 subjected to comb. 2 and to comb. 3 (around 0.800). This means that most of the Freundlich binding isotherms are fitted well.

Table 4 – Regression parameters for Freundlich isotherms.

		Freundlich		
		α	β	R ²
OPC	Comb. 1	4.916	0.774	0.967
	Comb. 2	5.170	0.631	0.928
	Comb. 3	4.719	0.818	0.988
HSR	Comb. 1	4.047	0.931	0.991
	Comb. 2	3.963	0.894	0.919
	Comb. 3	3.462	0.906	0.986
S50	Comb. 1	3.870	0.817	0.971
	Comb. 2	3.609	0.433	0.796
	Comb. 3	2.871	0.648	0.810

According to the binding isotherms, chloride binding decreases when the sulphate content increases. It is clear that this is valid for all concrete mixtures. Although the effect on the diffusion coefficients and the ccb is not always that clear.

CONCLUSIONS

- Resistance of concrete against chlorides is influenced by the temperature:

Temperatures below 20 °C result in a higher resistance against chlorides. Colour change boundaries as well as diffusion coefficients decrease when temperature decreases.

- The sulphate content of the aqueous chloride solution influences the resistance of concrete against chlorides only at high concentrations, namely higher than 27.5 g/l Na₂SO₄.

Overall, a sulphate content of 27.5 g/l Na₂SO₄ added to an 165 g/l NaCl solution has no pronounced influence.

For high sulphate resistant concrete the colour change boundary and diffusion coefficient do not vary much when Na₂SO₄ is added to a 165 g/l NaCl solution, even not when high amounts of sulphate are added. However, it should be mentioned that a small decrease in colour change boundary and diffusion coefficient is measured.

For ordinary Portland cement concrete and 50 % slag concrete immersed in a combined solution with high sulphate content, particularly of 55 g/l Na₂SO₄, results in an increase in colour change boundary.

Chloride binding decreases when the sulphate content increases. This is due to the binding of the sulphates with the C₃A.

- Overall, regardless the temperature, slag concrete has the best resistance against chlorides while concrete with high sulphate resistant cement has the lowest resistance. This effect is more pronounced at later age because of the slow hydration process of slag concrete.

REFERENCES

- [1] Tang L, "Chloride Transport in Concrete - Measurement and Prediction", Doctoral Thesis, 1996, Chalmers University of Technology, Göteborg
- [2] Shi C, Yuan Q, Deng D, Zheng K, "Test methods for the transport of chloride in concrete". Journal of the Chinese Ceramic Society, 2007, Vol. 35 (4), pp. 522-530
- [3] Matsumura T, Shirai K and Saegusa T, "Verification method for durability of reinforced concrete structures subjected to salt attack under high temperature conditions", Nuclear Engineering and Design, 2008, Nr. 238, pp. 1181-1188
- [4] Nguyen TS, Lorente S and Carcasses, "effect of the environment temperature on the chloride diffusion through CEM-I and CEM-V mortars: an experimental Study", Construction and Building Materials, 2009, Vol. 23, pp. 795-803

- [5] Otsuki N et al., "Temperature dependency of chloride induced corrosion in concrete", *Journal of Advanced Concrete Technology*, 2009, Vol. 7 (1), pp. 41-50
- [6] Glasser FP, Marchand J, Samson E, "Durability of concrete - Degradation phenomena involving detrimental chemical reactions". *Cement and Concrete Research*, 2008, Vol. 38 (2), pp. 226-246
- [7] Brown P, Hooton RD and Clark B, "Microstructural changes in concretes with sulfate exposure", *Cement and Concrete Composites*, November 2004, Vol. 26, pp. 993-999.
- [8] Sahu S, Badger S and Thaulow N, "Evidence of thaumasite formation in Southern California", *Cement and Concrete Composites*, June/August 2002, Vol. 24 (3-4), pp. 379-384.
- [9] Sahu S, Badger S and Thaulow N, "Mechanism of thaumasite formation in concrete slabs on grade in Southern California", *Cement and Concrete composites*, December 2003, Vol. 25 (8), pp. 889-897.
- [10] Brown PW, Hooton RD and Clark BA, "The co-existence of thaumasite and ettringite in concrete exposed to magnesium sulfate at room temperature and the influence of blast-furnace slag substitution on sulfate resistance", *Cement and Concrete Composites*, December 2003, Vol. 25 (8), pp. 939-945.
- [11] NBN EN 206-1, "Concrete – Part 1: specification, performance, production and conformity", European committee for standardization, Brussels, Belgium, 2000
- [12] NBN EN 196-2, "Chemical analysis of cement. Methods of testing cement". European committee for standardization, Brussels, Belgium, 2005
- [13] NBN EN 197-1, "Cement - Part 1: Composition, specifications and conformity criteria for common cement", European committee for standardization, Brussels, Belgium, 2000
- [14] NBN EN 12350-2, "Slump-test. Testing fresh concrete". European committee for standardization, Brussels, Belgium, 2009
- [15] NT Build 443, "Hardened concrete: Accelerated chloride penetration", Nordtest Method, 1995, p. 6
- [16] Yuan Q, "Fundamental Studies on Test Methods for the Transport of Chloride Ions in Cementitious Materials". Doctoral Thesis, 2009, Ghent University, Ghent
- [17] Pavlik V, "Water extraction of chloride, hydroxide and other ions from hardened cement pastes." *Cement and Concrete Research*, 2000, Vol. 30 (6), pp. 895-906