

CHLORIDE MIGRATION IN SELF COMPACTING CONCRETE

MIGRATION DES CHLORURES EN BETON AUTO-PLAÇANT

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ABSTRACT - Durability and more specifically chloride penetration, is of major importance for reinforced concrete structures. As the concept of self compacting concrete (SCC) is totally different from traditional concrete, some changes in durability behaviour might occur. In order to locate and prevent possible problems, the chloride penetration in SCC has to be investigated.

An extended experimental programme was set up: the chloride penetration of 16 self compacting concrete mixtures and 4 traditional concrete mixtures was determined. The test method is a non steady state migration test using an electrical field and was developed by Tang (1996) and described in NT BUILD 492. This test is carried out on the specimens at the age of 28, 56, 90 days, 1 and 2 years.

RÉSUMÉ – La durabilité et en particulier la pénétration des chlorures est très importante pour les structures en béton armé. Vu que la conception du béton auto-plaçant (SCC) est totalement différente comparée au béton vibré, certains problèmes concernant la durabilité peuvent se présenter. Afin de déterminer et prévoir les problèmes potentielles, il faut qu'on étudie la pénétration des chlorures dans le béton auto-plaçant.

Un programme expérimental approfondi est accompli: la pénétration des chlorures dans 16 bétons auto-plaçants et dans 4 bétons vibrés est déterminée à l'aide d'un essai de migration non stationnaire. L'essai utilisé se sert d'un champ électrique, a été développé par Tang (1996) et est décrit dans le document NT BUILD 492. L'essai est réalisé sur des éprouvettes à l'âge de 28, 56 ou 90 jours et 1 et 2 ans.

1. Introduction

Self compacting concrete (SCC) was developed in Japan in the 1980's. The aim was to develop a concrete with a high flowability and a high resistance to segregation, so that it could be placed without vibration. In this way, durability problems related with badly vibrated concrete would be reduced and some health risks as well as environmental problems could be avoided.

The high flowability (low yield value) is obtained by the use of powerful superplasticizers. A high amount of fine particles and in some cases a viscosity agent are added in order to reduce segregation and bleeding. Due to the presence of a high amount of fine particles, the pore structure is somewhat differing from the pore structure of traditional concrete. Because the pore structure is one of the major influencing factors concerning durability, the actual application of SCC might be somewhat riskfull due to the lack of knowledge concerning the actual durability of the new cementitious material.

Durability and more specifically chloride penetration, is of major importance for reinforced concrete structures. Before using self compacting concrete, the chloride

penetration has to be investigated in order to locate and prevent possible problems. In order to do so, an extended experimental programme was set up.

The chloride penetration of 16 self compacting concrete mixtures and 4 traditional concrete mixtures was determined. Four types of cement (portland cement and blast furnace slag cement), three types of filler (fly ash and two types of limestone filler with a different grading curve) and two types of coarse aggregate are used and the influence of the amount of powder and the amount of water is studied.

The test method is a non steady state migration test using an electrical field and was developed by Tang (1996) and described in NT BUILD 492. These tests are carried out on the specimens at the age of 28, 56, 90 days, 1 and 2 years.

From the migration tests, the diffusion coefficients were deduced. The decrease in time of the diffusion coefficients is studied and modelled based on models described in literature. A new model for the diffusion coefficient is proposed, based on the capillary porosity. This model is giving good results, both for traditional concrete and self compacting concrete.

2. Experimental programme

2.1 Concrete composition

At the Magne Laboratory for Concrete Research, 16 self compacting concrete mixtures (SCC) and 4 traditional concrete mixtures (TC) were investigated. In the first 9 mixtures a constant amount of cementitious materials (cement and filler) is considered: 600kg/m³, as well as a constant amount of water, sand and gravel, respectively 165k/m³, 853 kg/m³ and 698 kg/m³. Four types of cement are used (Portland cement CEM I 42.5 R, CEM I 52.5, CEM I 52.5 HSR and blast furnace slag cement CEM III A 42.5 LA), three types of filler (fly ash and two types of limestone filler BETOCARB P2 and Superfine S, the last one having a finer grading). In the next three mixtures, the amount of powder is varied (500 kg/m³, 700 kg/m³ and 800 kg/m³). In the following three mixtures, the amount of water is varied (144 kg/m³, 198 kg/m³ and 216 kg/m³). In SCC16 crushed limestone gravel was used instead of river gravel.

In the traditional concrete mixtures, three types of cement are used and the amount of cement is varied. The four traditional mixtures are corresponding with respectively the self compacting mixtures 1, 3, 6 and 4.

The amount of superplasticizer was determined in order to obtain a suitable flowability without segregation. Also the flowing time in the V-funnel was measured (values between 5s and 10s), air content (values between 1% and 3%) and the U-box requiring self levelling. In table I the mixture composition is given together with the slump flow and the compressive strength at 28 days measured on concrete cubes with side 150 mm.

Table I: Mixture composition

		CEM I 42.5 R [kg/m ³]	CEM I 52.5 [kg/m ³]	CEM III/A 42.5 LA [kg/m ³]	CEM I 52.5 HSR [kg/m ³]	limestone filler S [kg/m ³]	limestone filler P2 [kg/m ³]	fly ash [kg/m ³]	water [kg/m ³]	sand 0/5 [kg/m ³]	gravel 4/14 [kg/m ³]	Limestone gravel 2/14 [kg/m ³]	W/C [-]	C/P [-]	compressive strength [MPa]
SCC1	360				240		165	853	698		0.46	0.60	57.3		
SCC2		360			240		165	853	698		0.46	0.60	68.0		
SCC3			360		240		165	853	698		0.46	0.60	66.1		
SCC4				360	240		165	853	698		0.46	0.60	70.1		
SCC5	300				300		165	853	698		0.55	0.50	46.5		
SCC6	400				200		165	853	698		0.41	0.67	64.2		
SCC7	450				150		165	853	698		0.37	0.75	68.7		
SCC8	360				240		165	853	698		0.46	0.60	56.9		
SCC9	360					240	165	853	698		0.46	0.60	66.2		
SCC10	300				200		137	923	755		0.46	0.60	60.1		
SCC11	400				300		192	782	640		0.48	0.57	55.9		
SCC12	450				350		220	712	583		0.49	0.56	50.9		
SCC13	360				240		144	865	707		0.40	0.60	68.7		
SCC14	360				240		198	835	683		0.55	0.60	46.6		
SCC15	360				240		216	825	675		0.60	0.60	40.3		
SCC16	360				240		165	816		734	0.46	0.60	74.7		
TC1	360						165	640	1225		0.46	1.00	48.6		
TC2			360				165	640	1225		0.46	1.00	49.7		
TC3	400						165	626	1200		0.41	1.00	53.7		
TC4				360			165	640	1225		0.46	1.00	50.2		

2.2 Test method

From the mixtures described above, cubes 150 x 150 x 150 mm³ were made and were stored in a climate room at 20 °C ± 2 °C and more than 90 % R.H. At an age of 21 days, three cores with a diameter of 100 mm and a height of 50 mm were drilled from each cube. Afterwards the concrete cores were placed back in the climate room until the testing date (28, 56, 90 days or 1 or 2 years). On these cores a non steady state migration test was performed following the method of Tang and Nillson (1992). Firstly the specimens are vacuum saturated with a saturated Ca(OH)₂ solution. Afterwards an external electrical potential (for the tests described in this paper between 25 V and 40 V) is applied across the specimen for 24 hours and forces the chloride ions to migrate into the specimens. Afterwards the specimen is axially split and a silver nitrate solution is sprayed on to the freshly split sections. The chloride penetration depth can then be measured on each section at 7 points from the visible white silver chloride precipitation, after which the chloride migration coefficient can be calculated from these penetration depths with:

$$D = \frac{RT}{zFE} \frac{x - \alpha\sqrt{x}}{t} \quad \text{with: } E = \frac{U-2}{L} \quad \text{and } \alpha = 2\sqrt{\frac{RT}{zFE}} \operatorname{erf}^{-1}\left(1 - \frac{2c_d}{c_o}\right) \quad (1)$$

D is the non steady state migration coefficient (m^2/s), z the absolute value of ion valence, for chloride: z = 1, F the Faraday constant, F = $9.648 \times 10^4 \text{ J/(V.mol)}$, U the absolute value of the applied voltage (V), R the gas constant, R = 8.314 J/(K.mol) , T the average value of the initial and final temperatures in the anolyte solution (K), L the thickness of the specimen (m), x the average value of the penetration depths (m), t the test duration (s), erf⁻¹ the inverse of the error function, c_d the chloride concentration at which the colour changes, $c_d = 0.07 \text{ N}$ for Portland cement concrete, c_o the chloride concentration in the catholyte solution, $c_o = 2 \text{ N}$.

This method is using an electrical field to accelerate the penetration of the chlorides, which is not appearing in real circumstances. Therefore, the test results can only be considered qualitatively. However, the results are agreeing very well with test methods simulating real conditions (Audenaert (2005)).

2.3 Test results

In the figures 1 to 6 the migration coefficients are given for the concrete mixtures at the different ages. From these figures the following conclusions can be drawn:

- cement type (SCC1 – SCC2 – SCC3 – SCC4): a blast furnace slag cement results in a denser microstructure of the hydrated cement paste because more of the pore space is filled with C-S-H than Portland cement paste (4), resulting in a lower penetration depth and a lower migration coefficient.

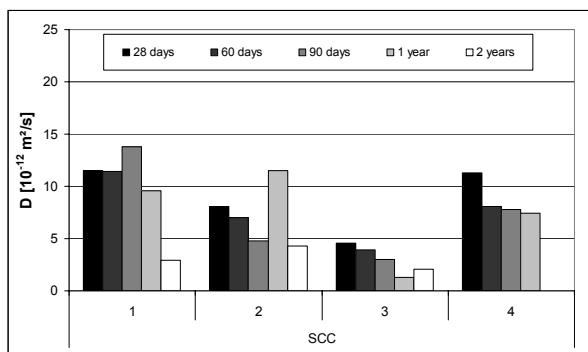


Figure 1: Influence of type of cement

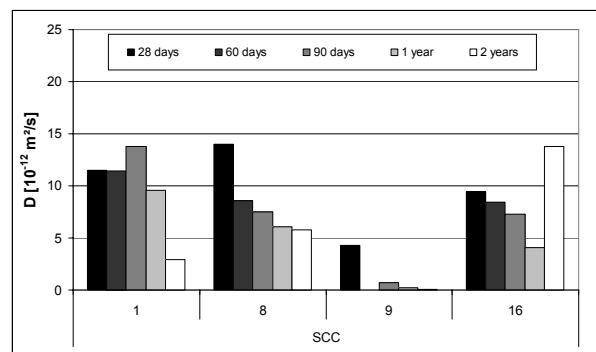


Figure 3: Influence of type of filler and coarse aggregate

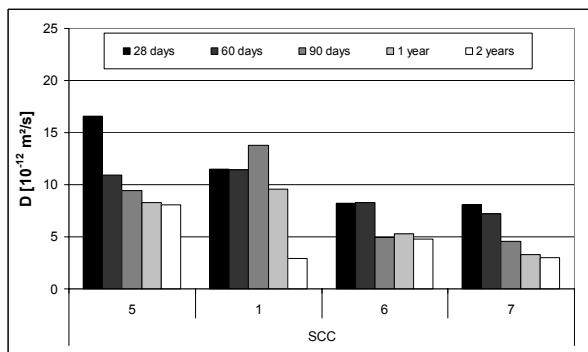


Figure 2: Influence of cement content

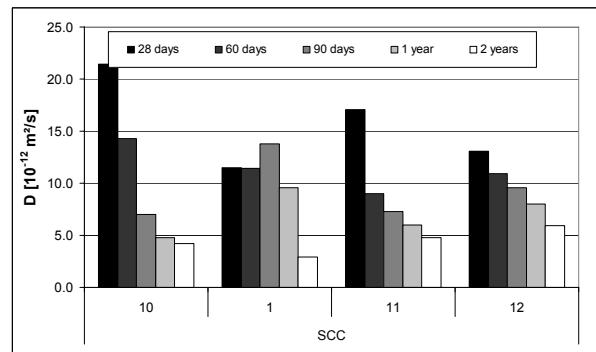


Figure 4: Influence of total amount of powder

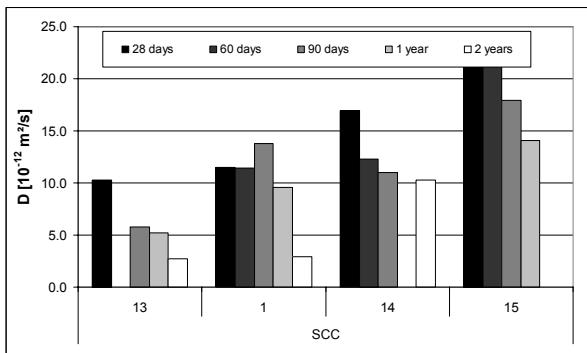


Figure 5: Influence of total amount of water

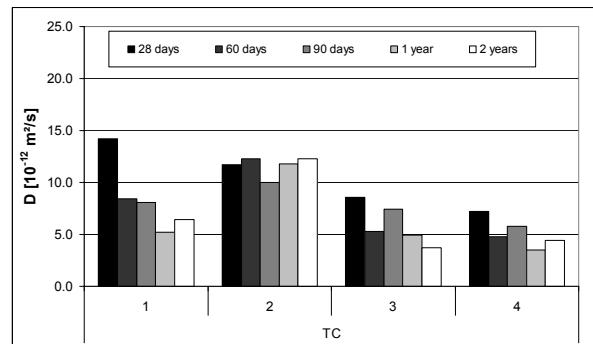


Figure 6: Comparison TC and SCC

- cement content (SCC5 – SCC1 – SCC6 – SCC7): the cement content of SCC5 is lower resulting in a higher W/C and W/P ratio and leading to a more open pore structure than SCC1. Thus the migration coefficient is higher at all testing times. The cement content of SCC6 and SCC7 is higher, resulting in a lower migration.
- type of filler (SCC1 – SCC8 – SCC9): a limestone filler with a finer grading curve was used in SCC8 possibly leading to a finer pore structure and to a lower migration coefficient. However the differences are small. SCC9 with fly ash has a lower migration coefficient caused by the very dense pore structure.
- type of coarse aggregate (SCC1 – SCC16): using a crushed limestone instead of river gravel leads to a stronger contact between the cement paste and the coarse aggregate, leading to a slightly lower chloride migration coefficient.
- total amount of powder with constant W/C and C/P ratio (SCC10 – SCC1 – SCC11 – SCC12): no clear conclusion can be drawn from the test results, so the influence of the total amount of powder (with constant W/C and C/P ratio) is small.
- total amount of water (SCC13 – SCC1 – SCC14 – SCC15): the amount of water of SCC13 is lower resulting in a lower W/C ratio and leading to a less open pore structure than SCC1. Thus the migration coefficient is lower at all testing times. The amount of water of SCC14 and SCC15 is higher resulting in a higher migration.
- TC in comparison with SCC: the migration coefficient for TC1 is very alike to the migration coefficient of SCC1. The same is valid for TC3 – SCC6. The migration coefficient of TC2 is significantly higher than the migration coefficient of SCC3. For TC4 – SCC4, it is the SCC mixture that has the largest migration coefficient.
- the chloride migration coefficient is decreasing in time. This decrease seems to be more pronounced for self compacting concrete.

3. Modelling

3.1 Introduction

In the modelling, several aspects should be taken into account:

- In the test results, the time dependency of the non steady state migration coefficient is clearly illustrated.
- With the CTH test, a non steady-state migration coefficient is determined. From these values a diffusion coefficient should be deduced.

- In literature it is written that the diffusion behaviour is depending on the capillary porosity. This dependency should be verified.

These three aspects will be discussed in the next sections.

3.2 Time dependency of diffusion coefficient

To evaluate the time dependent behaviour of the non steady state migration coefficient, tests were carried out at 28, 56, 90 days and 1 and 2 years. The time dependent behaviour is in literature (Costa (1999), Mangat (1994), Tang (2001)) mostly described by the next relation:

$$D(t) = D_1 t^{-m} \quad (2)$$

with D_1 the value at an age of 1 year and m a constant. The value of m was determined based on the test results of the self compacting and traditional mixtures, based on portland cement and without fly ash. For the three other mixtures the variation was too large and the number of test results too small to make a good prediction. This value is 0.27 and is corresponding very well with values in literature (Tang (2001), Bamforth (1999)).

3.3 Calculation of the diffusion coefficient

A possible calculation method to deduce the diffusion coefficient from the non steady state migration coefficient is proposed by the developers of the CTH-test in (Tang (1996)). This calculation method is also used in this research:

$$D_0 = D \left(1 + K_b \frac{W_{gel}}{\varphi_{cap}} \right) \quad (3)$$

with D the non steady state migration coefficient (m^2/s), D_0 the diffusion coefficient (m^2/s), K_b a binding constant ($\text{m}^3/\text{kg}_{gel}$), W_{gel} the amount of gel ($\text{kg}_{gel}/\text{m}^3_{concrete}$) and φ_{cap} the capillary porosity (-). For K_b values are given: for 100% portland cement $0.28 \cdot 10^{-3} \text{ m}^3/\text{kg}_{gel}$, for 30% blastfurnace slag and 70% portland cement $0.29 \cdot 10^{-3} \text{ m}^3/\text{kg}_{gel}$ and for 30% fly ash and 70% portland cement $0.32 \cdot 10^{-3} \text{ m}^3/\text{kg}_{gel}$.

For the calculation of W_{gel} the following equation is used:

$$W_{gel} = 1.25 h C \quad (4)$$

with h the degree of hydration (-) and C the cement content (kg/m^3). The test specimens are stored until the testing age in a climate room at $20^\circ\text{C} \pm 2^\circ\text{C}$ and at least 90% R.H. for at least 28 days. This means that the degree of hydration will not strongly differ from the ultimate degree of hydration, which could be determined by the Mill formula [van Breugel (1991)]:

$$h_{ultim} = \frac{1.031 \frac{W}{C}}{0.194 + \frac{W}{C}} \quad (5)$$

If the value of D_1 is used in formula (3) as non steady state migration coefficient, a value for the diffusion coefficient at the age of 1 year, D_{01} , is obtained.

3.4 Correlation between diffusion coefficient and capillary porosity

In literature, it is written that the transport properties of concrete are mainly determined by capillary pores (MC90 (1991), Marsh (1985), Audenaert (2006)). Therefore, the model of Powers (1946-1947) is used to determine the capillary porosity and this correlation is verified.

$$\begin{aligned}
 V_{\text{cap}} &= \text{capillary pores} + \text{free water} = \text{capillary pores} + \text{water} - \text{gel water} - \text{bounded water} \\
 &= 0.185 \frac{Ch}{\rho_c} + \frac{W}{\rho_w} - \frac{0.28}{0.72} \left(\frac{Ch}{\rho_c} (1 - 0.185) + \frac{0.23 Ch}{\rho_w} \right) - \frac{0.23 Ch}{\rho_w} \\
 &= -0.1319 \frac{Ch}{\rho_c} + \frac{1}{\rho_w} (W - 0.3194 Ch)
 \end{aligned} \tag{6}$$

with V_{cap} the volume of capillary pores [m^3], C the amount of cement [kg], W the amount of water [kg], h the degree of hydration [-], ρ_c and ρ_w the mass density of respectively cement and water [kg/m^3].

$$\begin{aligned}
 V_{\text{concrete}} &= V_{\text{water}} + V_{\text{cement}} + V_{\text{coarse aggregate}} + V_{\text{sand}} + V_{\text{filler}} \\
 &= \frac{W}{\rho_w} + \frac{C}{\rho_c} + \frac{A + S + F}{\rho_{\text{agg}}}
 \end{aligned} \tag{7}$$

$$\text{capillary porosity} = \frac{V_{\text{cap}}}{V_{\text{concrete}}} \tag{8}$$

with V_{concrete} the volume [m^3], A the amount of coarse aggregate [kg], S the amount of sand [kg], F the amount of filler [kg] and ρ_{agg} the mass density of aggregate [kg/m^3].

The parameters W, C, A, S and F are known from the mixture proportions. For the mass densities, a value of 1000 kg/m^3 is used for water, 2625 kg/m^3 for the aggregates, sand and filler and 3115 kg/m^3 for Portland cement. As degree of hydration, the ultimate degree of hydration is used, given in formula (5).

The obtained values of the diffusion coefficient at an age of 1 year are given in function of the calculated capillary porosity in Figure 7. A good correlation is obtained for self compacting concrete and for traditional concrete.

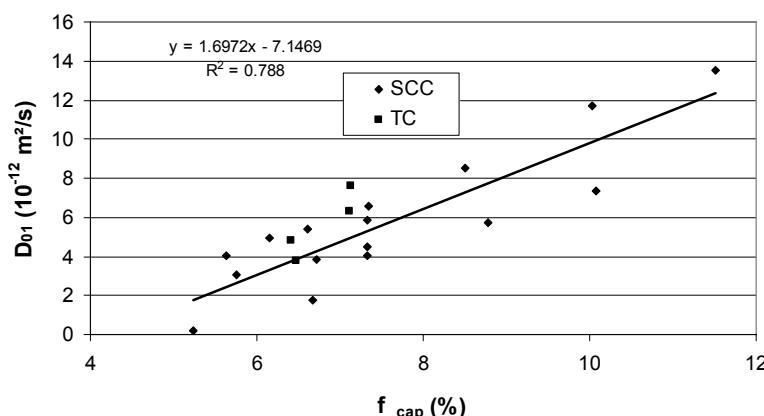


Figure 7: Diffusion coefficient in function of capillary porosity

4. Conclusions

The chloride migration coefficient of 16 self compacting concrete mixtures and 4 traditional concrete mixtures was determined with the non steady state migration test developed by Tang (1996) at the age of 28, 56, 90 days, 1 and 2 years. The following could be concluded:

- The chloride migration coefficient of self compacting concrete and traditional concrete decreases in time. This decrease seems to be more pronounced in case of self compacting concrete.
- The type of cement, cement content, type of filler, type of coarse aggregate and the total amount of water are the main influencing factors. The effect of changing the total amount of powder, keeping W/C and C/P ratio constant, is small.
- No clear conclusion can be drawn concerning the question whether self compacting concrete has larger chloride migration coefficients in comparison to traditional concrete.
- A model was proposed to deduce from a non steady state migration coefficient a diffusion coefficient, taking into the time dependent behaviour. This diffusion coefficient could be predicted based on the capillary porosity.

5. References

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