Chloride penetration into cementitious mortar at early age

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Modern service life design methods for concrete structures use chloride diffusion data as an input parameter. Abundant data exist for concrete at 28 days and, to a lesser extent, at later ages. This paper presents chloride diffusion data for mortar at ages between 1 day and 28 days age. Rapid Chloride Migration (RCM) and natural diffusion tests are performed on mortar specimens made with Portland (CEM I) and Blast Furnace Slag (CEM III/B) cement with w/c 0.50. The results show that mortar at a young age has a relatively high chloride migration coefficient. The value for CEM I at day 1 is one order of magnitude larger than at 28 days age, for CEM III/B this value is even two orders of magnitude larger. In the first two weeks, the value drops rapidly and more strongly for Blast Furnace Slag cement. The experimental data was used to model the chloride ingress up to 50 years with and without exposure to chloride at young ages. Modelling shows that the effect of exposure at young age is significant but relatively small when compared to the chloride ingress during the whole service life of concrete.

1 Introduction

The subject of this paper is the effect of early exposure to chlorides on durability of concrete. Early exposure might be important as the pore structure in young concrete is quite permeable. Therefore this study has looked at the effect on service life if a structure has to deal with a chloride load at early age.

The presence of chloride ions is not a problem for the concrete itself, but it may be for the embedded steel reinforcement. The passive oxide layer that normally forms on reinforcing bars in alkaline concrete can be destroyed by chloride ions. In this case pitting corrosion occurs: the cross section of reinforcing bars is reduced and corrosion products may cause cracking of the concrete cover or alternatively remain invisible for quite a long while [Bertolini et al. 2004].

This study focuses on the chloride transport process. The traditional approach is to consider the diffusion coefficient constant with time and place throughout the concrete. However, laboratory and field data suggest that the apparent diffusion coefficient decreases with time. Models have been developed that predict chloride penetration in time, taking into account an apparent chloride diffusivity that decreases with time [Maage et al. 1996], including the DuraCrete model [DuraCrete 2000].

It is usually assumed that diffusion governs the ingress with the concentration gradient as the driving force. The description of non-steady state diffusion was stated by Fick,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x} \right), \qquad (1)$$

where
D = diffusion coefficient (m^2/s),
c = chloride content by (% by mass of cement or concrete),
x = depth from the surface of concrete (m),
t = time (s).

For the non-steady situation, Crank's solution of Equation 1 is used [Crank 1975],

$$c(x,t) = c_0 \left(1 - erf\left(\frac{x}{2\sqrt{Dt}} \right) \right), \qquad (2)$$

where $c(x, t)$ is the chloride content as a function of time and place, c_0 is the surface chloride content and *erf* is the error function. However, Crank´s solution for penetration with constant diffusion coefficient is not valid when the coefficient is time dependent. In this case the solution of the problem should start with the differential Equation 1. With the objective of obtaining data and a model for $D(t)$ a study of diffusion coefficient values for concrete at early ages was carried out and will be described in this paper.

2 Experimental

The objective of the experiments was to obtain diffusion coefficient values for early ages. At this moment most values found in the literature are taken at ages of 28 days and longer. In this research, tests were performed on concrete mortars containing CEM I 32.5 R and CEM III/B 42.5 N, with a cement-sand ratio of 1 : 3 and a water-cement ratio of 0.5. Specimens were cast cylinders with a diameter of 100 mm and a height of 50 mm. Three tests were performed on these specimens: Rapid Chloride Migration (RCM), natural diffusion and electrical resistivity.

The RCM test was performed according to NT Build 492. This is an accelerated test that can be executed in a short period of time (hours to days), such that it may be thought to produce an instantaneous diffusion coefficient. The test procedure, however, had to be adapted for samples of this particular young age. Vacuum saturation, which is part of the standard procedure, can damage the young microstructure; keeping the specimens under water serves the same purpose: to prevent drying out. Thus, samples were submerged in a saturated $Ca(OH)_2$ solution immediately after casting until the RCM took place.

The chosen ages for RCM testing were 1, 2, 3, 7, 14, 21 and 28 days. The testing frequency was higher in the first week as the diffusion coefficient was expected to change more strongly during this period. The weekly interval between 7 and 28 days was thought to produce enough data to analyse the trend at later ages. The value at 28 days is especially interesting because this provides a validation point to previous tests that are reported in literature. Three specimens were tested for each age and type of cement.

The second test method was the natural diffusion test, based on NT Build 443. Again, the test method was adapted slightly to accommodate the high permeability of the young samples. The main deviation from the standard procedure was the duration of the exposure. Specimens were not exposed for the standard duration of 35 days, as very deep penetration could be expected. Consequently, exposure durations were reduced to lengths that were expected to produce around 10 - 15 mm penetration. The program consisted of three tests for each mixture (single specimen), covering the first sixteen days of age, where the largest changes in properties occur (on the basis of RCM results). The tests were started at ages 1.5, 3 and 7 days with exposure times of 3, 5 and 9 days, respectively. These tests were not accelerated, therefore the period of testing was longer. After the exposure, six layers of two millimetres thickness were ground off the sample starting at the exposed face. A vacuum hose was used to collect the dust; after dissolution in nitric acid, chloride analysis was carried out using Volhard's titration.

Finally electrical resistivity measurements are performed using the two electrode method (TEM) [DuraCrete 2000]. In this test the AC resistance (120 Hz) between two flat electrodes on either side of cylindrical specimens is measured. The resistivity reveals how easy it is for charges to move through a porous material. Although this is not the same as chloride diffusivity, it does provide an indication of the mobility of chloride ions [Polder 2000]. Therefore measurement of the electrical resistivity is a simple way to characterize the microstructure development and therefore the development of its resistance against chloride penetration. Measurements were made for all specimens before and after the RCM tests. The electrical resistivity of the mortars was calculated by [Polder 2000]:

$$\rho_{mortar} = R\frac{A}{L}, \qquad (3)$$

where ρ_{mortar} is the electrical resistivity (in Ωm), R is the electrical resistance of the sample (in Ω), A the surface area (in m^2) and L the length of the specimen (in m).

3 Experimental results and discussion

The RCM results are reported in Table 1. The evolution of the instantaneous diffusion coefficient with time can be observed in Figure 1. Values show a fast drop during the first days, with one day old samples having much higher values than more mature samples. The value for CEM I at day 1 is one order of magnitude larger compared to the value at 28 days age, and for CEM III/B this is even up to two orders of magnitude larger. CEM I samples appear to have a larger standard deviation than CEM III/B samples. This is

Table 1: Mean and standard deviation for diffusion coefficient D_{RCM} in 10^{-12} m^2/s as a function of age at testing

	CEM I		CEM III/B	
Age (day)	Mean	Stdev	Mean	Stdev
1	160	16	310	2
2	65	10	82	3
3	37	14	68	5
7	21	8	26	8
14	19	11	4	2
21	18	3	3	1
28	17	1	3	2

probably not a real effect, but rather due to execution issues. In Figure 1 it can be seen that the D_{RCM} value for CEM I starts lower and drops quicker to even lower values in the first week compared to CEM III/B; however in in the next week, the D_{RCM} value for CEM III/B declines at a faster rate. In the logarithmic plot in Figure 2 the trend for both mixtures during the first week appears to be the same, represented by more or less parallel lines. This suggests similar processes, probably hydration of Portland clinker. From about one week age, the development of CEM I is slow, but for CEM III/B a new process appears to happen. The variation of the diffusion coefficient is steeper, which is probably due to the refinement of the pore structure caused by hydration of blast furnace slag. Blast furnace slag cement is known for having a high resistance against chloride penetration [Bertolini et al. 2004, Polder 1996]. This is attributed to the dense

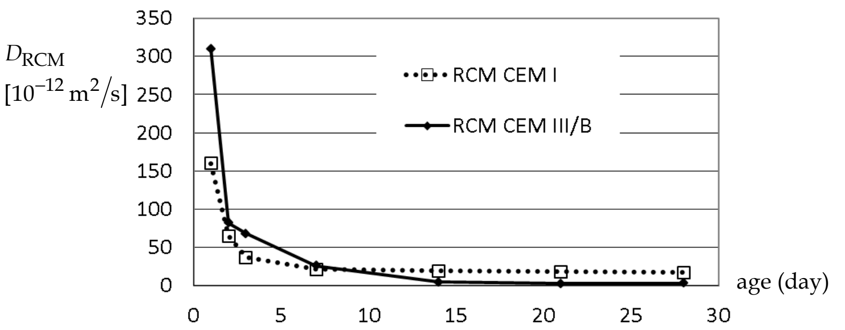

Figure 1: Evolution of instantaneous diffusion coefficient (RCM) with time

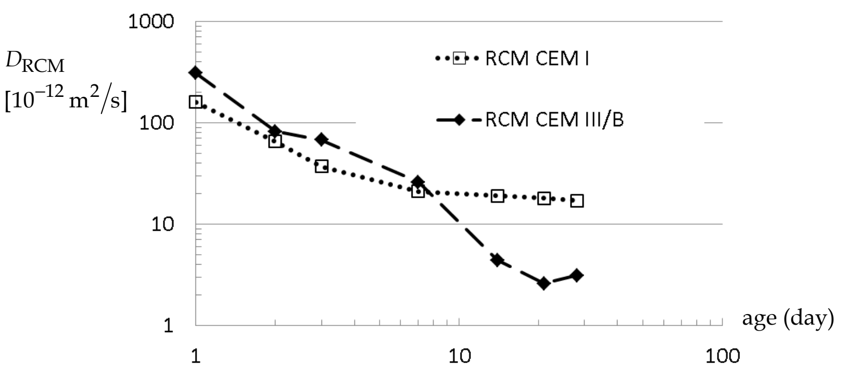

Figure 2: Logarithmic evolution of instantaneous diffusion coefficient (RCM) with logarithm of time

microstructure which this cement produces, through which chlorides cannot easily pass. The test results show that, in a general sense, for CEM III/B it takes around 14 days to reach a resistance against chloride penetration that approaches the 28 days value, whereas for CEM I this level is reached in seven days. If both mixtures are compared, the microstructure in early CEM III/B develops more slowly and therefore the values of the diffusion coefficient decrease more slowly. Diffusivity at early age is higher (compared to the mature state) and remains high for a longer time. A stronger influence is consequently expected of early exposure for CEM III/B.
Chloride concentration profiles were obtained after the natural exposure to chlorides. A mathematical fit to Crank's solution given in Equation 2 was made to obtain apparent diffusion coefficients and surface chloride concentrations. Results are reported in Table 2. If compared to the D_{RCM} values it can be seen that the measured D_{app} at 1.5 to 4 days is around the measured values of day 3 for both cement types and the measured values drop significantly over the first two weeks. This affirms the results of the accelerated RCM tests.

Table 2: Results of natural diffusion tests; apparent diffusion coefficients D_{app} are expressed in 10^{-12} m^2/s and chloride surface concentrations C_s in % by mass of cement.

Exposure interval (day)		1.5-4	3-8	7-16
CEM I	C_s	9.4	9.6	6.7
	D_{app}	38	22	18
CEM III/B	C_s	10	11.7	9.6
	D_{app}	63	29	5

Table 3: Resistivity values in Ωm

Age (day)	CEM I	CEM III/B
1	8	7
2	14	14
3	17	22
7	28	136
14	30	150
21	29	180
28	30	254

TEM Resistivity results are shown in Table 3. These measurements were taken before the RCM tests and therefore the values are not affected by the presence of chlorides. These results express the further development of the microstructure for CEM III/B when compared to CEM I.

4 Modelling

The tests provided data about the development of the properties needed to solve a chloride ingress problem. Thus, a model was created that describes the apparent diffusion coefficient during the complete life of the material, from early age on, which then was used to solve the differential equation that describes the penetration of chloride (Equation 1). The model uses the presented RCM results for young ages and RCM values found in literature for older ages. The model therefore consists of two parts, one coinciding with the short term ingress, the other with the long term ingress. For the part that models early age, a mathematical fit was made to the RCM data with a mathematical equation as presented in Equation 4. The reason to choose this type of equation is that the behaviour is essentially the same (exponential) as in e.g. [Maage et al. 1996, DuraCrete 2000], but some coefficients (a, b, d) are added to get a closer approximation of the data. This proposed model can be used for both cement types. It should be noted that the parameters are a result of a mathematical data fit and do not have a physical meaning.

$$D(t) = \frac{a}{(t+b)^c} + d \,, \tag{4}$$

Here, t represents the age of the samples expressed in days. The output is the apparent diffusion coefficient in m^2/s. The range of application of these formulas is strictly the interval between 1 and 28 days. In order to complete the model, the behaviour for ages older than 28 days must also be captured in an equation. This part of the model follows DuraCrete [see also Wegen, et al. this issue], in which the time dependent apparent diffusion coefficient has the expression as given in Equation 5.

$$D(t) = D_0 \left(\frac{t_{ref}}{t} \right)^n \,, \tag{5}$$

Here, t_{ref} is a reference age, D_0 is the RCM diffusion coefficient at that age and n describes the evolution with time, being a characteristic of material and environment [DuraCrete 2000, Wegen et al. this issue]. Most of the information found for D(t) is for apparent diffusion coefficients, which have been derived from fitted profiles. One of the findings from previous work is that the value for n is higher for CEM III/B than for CEM I concrete [DuraCrete 2000, Wegen et al. this issue, Polder 1996]. For the present modelling, RCM values for mature mixtures with similar compositions are needed. These values were obtained from [Visser & Polder 2006] in which water saturated samples up to 3 years of age were tested with RCM and n was fitted with Equation 5. It was assumed that concrete and mortar have the same diffusion coefficient. This is not completely correct (see [Bouwmeester-Van den Bos et al. 2010]), but differences are relatively small and can be neglected for the present purpose. To create continuity in the model it was decided to maintain the parameter n calculated from [Visser & Polder 2006], which is a characteristic of the material and describes the evolution of the diffusion coefficient with time. D_0 was chosen to be the 28 day value of D_{RCM}. The accuracy in this second part of the model is not the main concern, since the aim is not obtaining exact profiles but to study the influence of early exposure.

The values for the model parameters that are needed for both the short and long term parts of the model are presented in Table 4. In the future it would be worthwhile to look for one mathematical model that can represent the whole timeframe.

Table 4: Model for apparent chloride diffusion coefficient D(t) in 10 -12 m²/s

	Age < 28 days	Age ≥ 28 days
CEM I	$\left(\frac{181}{(t+0.3)^{1.62}}\right)+16$	$17\left(\frac{28}{t}\right)^{0.3}$
CEM III/B	$\left(\frac{330}{(t+0.5)^{1.5}}\right)-1.1$	$3\left(\frac{28}{t}\right)^{0.4}$

A Matlab program was developed to solve the differential equation 1. The criteria to evaluate differences in "service life" were the following: It was assumed that a value of 0.5% chloride content by mass of cement would cause corrosion initiation of reinforcement, which was regarded to represent the end of service life. The difference in time between early (e.g. one day) and mature exposure (e.g. 28 day) to reach 0.5% at 50 mm depth is considered. A chloride concentration of 3% in the surface of the sample was used, typical for marine splash zone exposure XS3 [Wegen et al. this issue, Polder & Rooij, 2005].

One way to analyse the effect of early exposure is to compare concentration profiles after a certain length of exposure that has started at different ages. In the studied case of CEM III/B there is a difference of 1.4 mm in depth where the threshold of 0.5% is reached after fifty years. So in a structure exposed at one day to chloride, the critical chloride content has travelled 1.4 mm further, compared to a structure that is loaded with chloride at 28 days. This is shown in Figure 3.

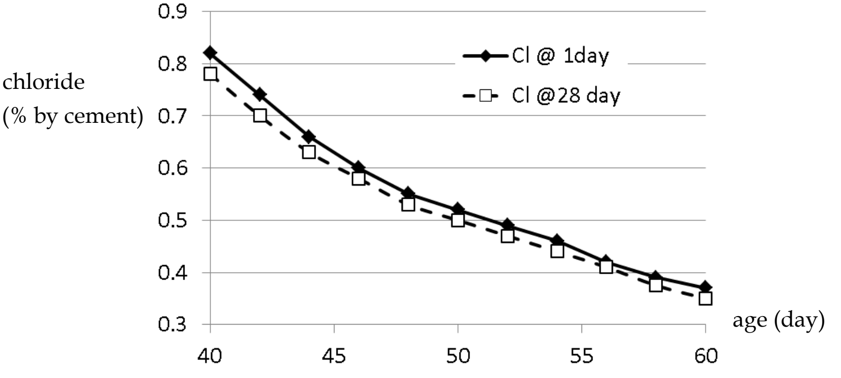

Figure 3: Differences around 50 mm of early and mature exposure after 50 years

In order to obtain differences in service life (time to corrosion initiation) the differences in chloride concentration have to be turned into differences in time. This was done by letting the “mature exposure” profile evolve for an additional period until the chloride threshold was reached at the same depth as for “early exposure” (48.5 mm).

In the case studied here, and based on the results after fifty years, the “28 days” profile would need an additional 4.25 years to reach the threshold at 48.5 mm. This means that if the reinforcement were at 48.5 mm, the corrosion would start more than four years later if early exposure was avoided (that is, exposure would start at 28 days instead of at 1 day age).

As the RCM results show a steep decrease of the diffusion coefficient during the first week, it was thought interesting to see how postponing the first contact with chlorides, from one day to 15 days, affects the service life. Again CEM III/B will be used for this case. If a cover depth of 50 mm is considered, the exposure times at which 0.5% chloride is reached for the different starting times can be calculated. By comparing the times, the effect of a delay of the first exposure can be studied. The results are shown in Table 5. It appears that some effect can be obtained by avoiding chloride exposure in the very first days. The most significant saving occurs if the first contact is delayed from the first day to the second day: one day delay of exposure at early age results in nearly two years more service life. It should be noted that the specimens studied here were kept moist. Consequently, the results and interpretations apply only if the concrete is well cured until contact with chloride. Various studies show that curing is important to obtain a good resistance against chloride transport but also against carbonation and freeze/thaw attack, in particular for blast furnace slag cement concrete [Bouwmeester-Van den Bos et al. 2010, Copuroglu et al. 2004].

Table 5: Effect on the service life of delaying the first exposure to chloride

Start of exposure at age (day)	Years to reach 0.5% at 50 mm depth	Difference with start of exposure at one day age (years)
1	53	0
2	55	1.8
4	56	3.2
8	57	4.2
15	58	5

5 Conclusions

Some conclusions can be drawn on the basis of the test results and the modelling. Diffusions tests performed on young mortar made with two cement types show very high chloride diffusion coefficients.

The effect of cement type is significant and mortar made with CEM III/B presents higher values of diffusion coefficient at early ages than mortar made with CEM I. At seven days, the diffusivity for both mixtures is similar. For ages above seven days CEM III/B has lower diffusion coefficients. The diffusion coefficient evolution with time for both mixtures shows that the effect of early exposure to chlorides is more significant for CEM III/B.

In order to study the effect of the high early diffusion coefficient a model was developed that was used to simulate chloride ingress through time with and without early exposure to chlorides.

Calculations for some practical cases with typical parameters show that the effect of early exposure to chlorides can be of importance if the structure is exposed to chlorides at the age of one day, as opposed to start of exposure at 28 days (which is usually assumed). In that case, the time to corrosion initiation for CEM III/B is around 4 years or 10% shorter.

Further calculations show that avoiding contact with chloride during the first days improves the time to corrosion initiation significantly. In the case studied, postponing the start of exposure from day 1 to day 2 increases the time to initiation by about 2 years or 5%. These predictions should be rather seen as relative than absolute in view of the inaccuracies of the model used and uncertainties in life predictions in general.

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