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Fagerlund, Göran

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IMAGINABLE EFFECTS OF LIMESTONE FILLER ON CHLORIDE TRANSPORT

Göran Fagerlund

Contents

List of symbols

C	Cement content in mix (kg per m^3 of concrete)
C′	Cement content (g per cm^3 of concrete) (Note: $C′=10^{-3}·C$)
F	Amount of limestone filler (kg per m^3 of concrete)
K	Steady state chloride diffusion coefficient at 100% porosity (m^2/s)
P_{cap}	Capillary porosity (m^3 per m^3 concrete or cement paste)
P_{tot}	Total porosity (m^3 per m^3 concrete or cement paste)
P_w	Water-filled porosity (m^3 per m^3 concrete or cement paste)
Q_{bound}	Amount of bound chloride in a specimen (g)
Q_C	Cement content in a specimen (g)
Q_{free}	Amount of free chloride in a specimen (g)
Q_{gel}	Amount of hydration products ("cement gel") (kg per m^3 concrete)
$Q_{gel}′$	Amount of hydration products ("cement gel") in a specimen (g)
Q_{tot}	Total chloride in a specimen (g)
R	Ratio between bound and free chloride defined by $R=c_b/c$ (-). Note: $R≠c′_b/c′$.
W	Water Content in fresh mix (kg per m^3 of concrete)
W_p	Total amount of pore water (m^3 per m^3 of concrete)
$W_{p,cap}$	Amount of capillary pore water (m^3 per m^3 of concrete)
W_w	Amount of pore water dissolving chloride (m^3 per m^3 of concrete)
V	Specimen volume (m^3)
c	Concentration of free chloride in concrete or in a bath surrounding a specimen (kg per m^3 water)
c′	Amount of free chloride (kg per m^3 of concrete)
c′′	Concentration of free chloride (g per litre pore water). (Note: $c′′=c$)
c′′′	Concentration of free chloride (g per cm^3 pore water). (Note: $c′′′=10^{-3}·c$)
c_b	Amount of chloride extracted from pore water by chemical and physical binding to the solid material (kg per m^3 pore water)
$c_b′$	Amount of bound chloride (kg per m^3 of concrete)
$c_b′′$	Amount of bound chloride (mg per g cement). (Note: $c′′_b=10^3·c_b′/C$)
$c_{b,gel}$	Amount of bound chloride in the cement gel (g per g gel, or kg per kg gel)
$c_{tot}′$	Sum of bound and free chloride –total chloride (kg per m^3 of concrete)
$c_{tot,s}′$	Total chloride at the exposed surface (kg per m^3 of concrete)
k	Efficiency factor of limestone filler (-)
q	Flow of chloride ions (kg per m^2)
r	Ratio between filler and cement (-)
t	time (s)
vbt_C	Water-binder ratio with only cement in the mix (-)
vbt_F	Water-binder ratio with filler in the mix (-)
w_w	Amount of water dissolving chloride in a specimen (g=cm^3)
$w_{w,cap}$	Amount of capillary water in a specimen (g=cm^3)
$w_{w,tot}$	Total amount of water in a saturated specimen (g=cm^3)
x	Distance from chloride exposed surface (m)
α	Degree of hydration (-)
γ	Coefficient describing amount of pore water dissolving chloride- equation (17) (-)
$δ_0$	Diffusion coefficient of chloride ions with no binding "steady state" diffusion coefficient (m^2/s)
$δ_{eff}$	Effective diffusion coefficient of chloride (m^2/s)

1 Introduction and summary

There is some experimental evidence that the addition of limestone filler to concrete with unchanged water-cement ratio might increase the chloride ingress in concrete; e.g. Persson (2001) and Boubitsas (2005). This means that the filler has, what can be called, a negative "efficiency factor" with regard to chloride uptake, in contrast to other reactive fillers (mineral admixtures) such as fly ash and ground granulated blastfurnace slag. This negative effect might occur also when limestone filler is used in self-compacting concrete, Persson (2001).

The efficiency factor of a mineral admixture, like filler, with regard to chloride diffusivity expresses the amount of ordinary cement that can be replaced by a given amount of filler at unchanged diffusivity. In case of limestone filler no cement can be replaced. On the contrary, *more cement has to be added in order to maintain the same resistance to chloride uptake.*

The definition and calculation of the efficiency factor is illustrated by Figure 1. δ_{eff} is the effective diffusion coefficient, see equation (4).
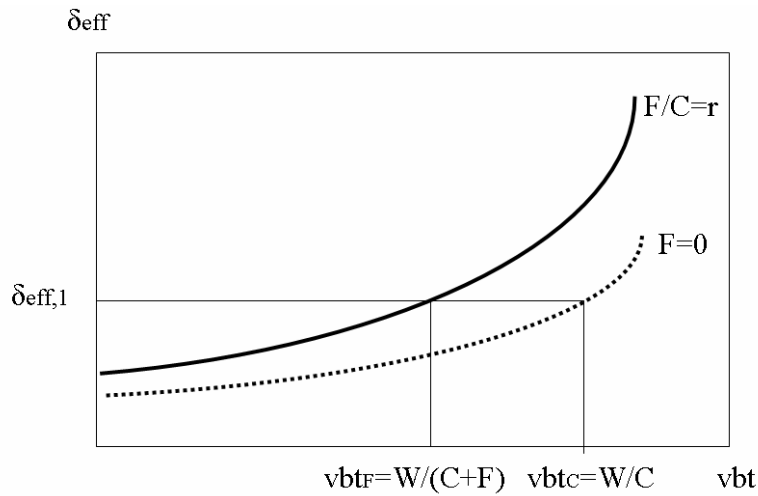
Figure 1: Illustration of the efficiency factor.

With filler the water-binder ratio for a given diffusivity is: $vbt_F = W/(C+F) = W/C(1+r)$

Without filler the required water-cement ratio for the same diffusivity is: $vbt_C = W/C$

The same effective diffusion coefficient as for concrete with pure cement is also obtained for the concrete with filler if an effective water-binder ratio is used: $vbt_{F,eff} = W/C(1+k\cdot r)$.

Where k is the *efficiency factor*. This is obtained by combination of the expressions above:

$vbt_F = W_1/[C_1(1+r)]$ where W_1 and C_1 are the water content and cement content in concrete with filler. Thus $W_1/C_1 = vbt_F(1+r)$.

By definition, $vbt_{F,eff} = W_1/C_1(1+k\cdot r) = vbt_C$. Inserting $W_1/C_1 = vbt_F(1+r)$ and redistributing the terms gives:

k=[vbt_F(1+r) -vbt_C]/vbt_C·r (1)

Example 1
For a given chloride diffusivity a water-cement ratio $vbt_C=0.4$ is needed when there is no filler in the concrete.

For the same chloride diffusivity a water-binder ratio $vbt_F=0.3$ is needed when the concrete contains 20% filler (r=0.20).

The efficiency factor becomes: $k=[0.3(1+0.20)-0.4]/0.4\cdot0.20=$ **-0.50**

The negative efficiency factor means that more cement is needed for maintaining the same chloride diffusivity.

Example 2
The same as Example 1.
The efficiency factor -0.50 can be used for calculating the extra cement.
The amount of mixing water is assumed to be 170 l/m^3.
Cement content with no filler: $C_0=170/0.4 =$ **425 kg/m^3**
Cement content with 20% filler (provided filler does not change the required water content for constant workability):
$C_1= 170/[0.4(1-0.5\cdot0.2)]=$ **472 kg/m^3**

In the report a discussion is carried out on factors determining chloride ingress in concrete and on possible effects of limestone filler on these factors.

In paragraph 2, the difference between the "steady state" chloride diffusion coefficient and the effective chloride diffusion coefficient is pointed out. The relation between the two coefficients is described by the ratio R between the bound chloride, which is extracted from the pore solution, and the free chloride, which is remaining in the pore solution; equation (3).

In paragraph 3, a limited literature review of the relation between bound and free chloride is performed. Some measurements indicate that there is a linear relationship, other measurements that the relationship is non-linear. In both cases it is found that the relation is a function of the water-cement ratio; the higher the w/c-ratio, the lower the fraction of bound chloride. Furthermore, some results indicate that the fraction of bound chloride decreases with increased alkalinity of the pore solution.

Experiments indicate, quite reasonably, that the fraction of bound chloride is directly proportional to the amount of hydration products.

Theoretical analyses of the effect of water-cement ratio and concrete age on chloride binding and transport, using the linear relation between bound chloride and amount of hydration products, are carried out in **ANNEX 1** and **ANNEX 2**.

In ANNEX 1 it is shown that the coefficient R describing chloride binding decreases with increased w/c-ratio and increases with increased degree of hydration.

In ANNEX 2 it is shown theoretically that the effective coefficient of chloride diffusion increases linearly with increasing w/c-ratio. This is in accordance with experiments.

In paragraph 4, a hypothesis is put forward that the negative effect of limestone filler might depend on a reduced chloride binding capacity caused by reaction between the filler and chloride-binding components in the cement, mainly C_3A.

An additional explanation could be that the filler causes increased "steady state" chloride permeability due to structural changes of the cement paste. This explanation is less probable, however, since the main reaction products determining the pore structure are the calcium silicates, and the reaction products of these are hardly affected by limestone filler.

In paragraph 5, methods for investigating mechanisms behind the effect of limestone filler on chloride transport are suggested. The effect on the basic properties *steady state diffusion coefficient* (denoted δ_0 in equation (2)) and *chloride binding capacity* (denoted $R=c_b/c$ in equation (4)) should be investigated. Suggestions for test methods are given. Evaluation techniques are presented in **ANNEX 3** and **ANNEX 4**.

2 The chloride diffusion coefficient

2.1 Without chloride binding

Uni-directional transport of chloride ions into the pore space of a concrete specimen stored in a solution containing chloride ions is in the simplest way described by (Fick´s second law):

$$\mathbf{dq/dt = \delta_0 \cdot d^2c/dx^2} \tag{2}$$

where q is the ion flow in one square-meter of concrete (kg/m^2), δ_0 is the diffusion coefficient (m^2/s), c is the chloride concentration in the pore water (kg per m^3 pore water), x is the coordinate along the flow axis (m).

This equation is based on the assumption that there is no chemical or physical binding of chloride ions. The diffusion coefficient δ_0 can be determined in a steady state test in which a thin slice of the concrete is placed as a partition wall between two chambers; one, initially containing a chloride-free solution, and the other containing a solution with chloride; see Figure 8. The chloride transport rate is evaluated from frequent chloride analyses of the liquid in the two chambers. The transport coefficient is obtained when steady state flow has been reached.

2.2 With chloride binding

A certain fraction of chloride ions is bound in concrete, mostly chemically in the hydration products, but also physically to the pore walls. As a first approximation it is assumed that binding is linear, i.e. the amount of chloride extracted from the pore water, c_b, by binding (kg per m^3 pore water) is directly proportional to the amount of free chloride left to migrate in the pore water, c (kg per m^3 pore water):

$$\mathbf{c_b = R \cdot c} \tag{3}$$

where R is the proportionality coefficient (-).

> *Note:* R is a *dimensionless* entity, since the bound chloride is expressed in terms of chloride *extracted from* the pore solution. Thus, in order to calculate R the chloride in the pore solution must be re-calculated to the same unit as the bound chloride, e.g. kg/m^3 of concrete, or the bound chloride must be re-calculated to the same unit as the free chloride, e.g. kg/m^3 of pore solution. In both cases, this means that the volume of pore solution must be known.

Chloride transport can now be formulated:

$$dq/dt = \delta_0 \cdot d^2c/dx^2 - dc_b/dt \tag{4}$$

Inserting eq (3) gives:

$$\mathbf{dq/dt = [\delta_0/(R+1)] \cdot d^2c/dx^2 = \delta_{eff} \cdot d^2c/dx^2} \tag{5}$$

Where $\mathbf{\delta_{eff} = \delta_0/(R+1)}$ is an *effective diffusion coefficient* valid under non-steady state conditions (m^2/s).

The effective diffusion coefficient δ_{eff} can be calculated from the measured *profile of total chloride* c_{tot}' (the sum of free and bound chloride) reached in a specimen after a known exposure time in a chloride solution with constant concentration. The solution to equation (5) is used with the free concentration c exchanged for the total concentration c_{tot}'.

$$c_{tot}'/c_{tot,s}'=1\text{-}erf[x/(4\cdot\delta_{eff}\cdot t)^{1/2}] \tag{6}$$

where c_{tot}' is the measured total amount of chloride (kg per m^3 concrete -or kg per kg concrete, or kg per kg cement) on the distance x (m) from the surface after the exposure time t (s). $c_{tot,s}'$ is the total amount of chloride at the surface part of concrete. erf is the "error function". A table over the error function can be found in Crank (1985).

Since the surface amount of chloride is impossible to determine experimentally, one can instead use the measured concentration $c_{tot,1}'$ and $c_{tot,2}'$ on two different depths, x_1 and x_2. From the two measurements both the value of $c_{tot,s}'$ (a fictitious value) and δ_{eff} can be evaluated. By using many interlinked values $c_{tot,i}'$ and x_i a more accurate value of δ_{eff} is of course obtained.

The *profile of free chloride* c´ (kg per m^3 concrete) can be calculated from the profile of the total chloride by using equation (3) expressed as:

$$c' = c_{tot}'\text{-}c_b' =c_{tot}'/(1+R) \tag{7}$$

Thus, in order to obtain the profile of free chloride, expressed in terms of kg per m^3 of concrete, c´, the bound total chloride profile is divided by a constant factor (1+R).

For obtaining the concentration of free chloride in the pore water c (kg per m^3 pore water), c´ is divided by the amount of pore water dissolving chloride, W_w (m^3 per m^3 of concrete):

$$c=c'/W_w \tag{8}$$

Note: In reality the relation between free and bound chloride is not always linear; see next paragraph. This means that equations (4) to (6) do not give a correct description of chloride transport. Chloride transport with non-linear chloride binding is treated in Tang (1996).

3   Bound and free chloride

3.1 Introduction

The relation between free and bound chloride is not very well known. One of the first to make experimental determinations of the relation was Tuutti (1982). He used so called pore pressing to analyse the free chloride content, and chemical analysis for determination of the total chloride content. The relations between free and bound chloride he found were linear; Figure 2 and 3. Linear relations have also been obtained in research by Arya & Newman (1990).

In other investigations, non-linear binding has been observed, Sandberg & Larsson (1993), Tang & Nilsson (1993); Figures 4 and 5. These measurements were made with another technique in which the material was stored for so long time in chloride solution that there was equilibrium between the chloride concentration in the pores and the outer solution, see Figure 9. Analysis of the total chloride content and pore volume made it possible to calculate both free and bound chloride.

Some examples of relations between free and bound chloride are given below.

3.2 Linear relation

Examples of linear relations between bound and free chloride are shown in Figure 2 and 3; Tuutti (1982). The cement is a high alkali OPC with about 8% C_3A.
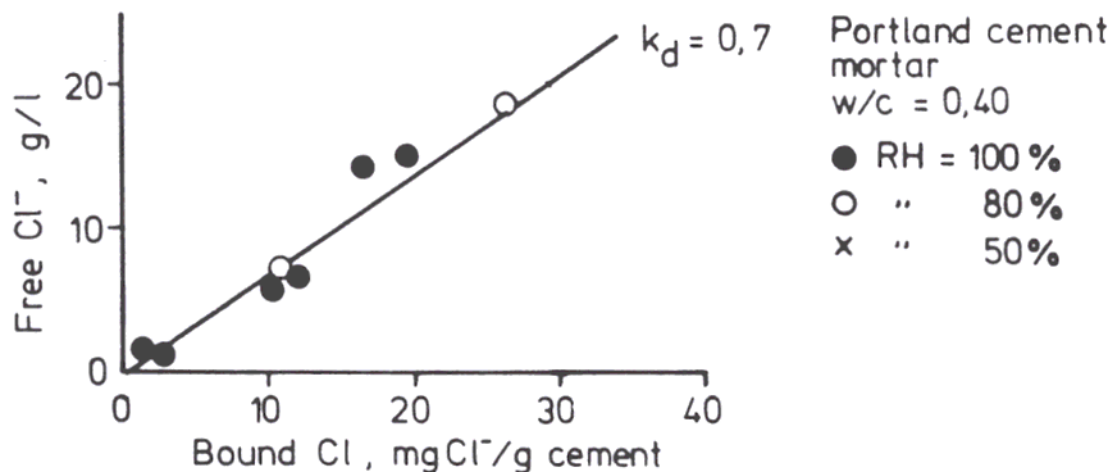

Figure 2: Relation between free (c´´), and bound (c_b´´) chloride. w/c 0.4. Tuutti (1982). Specimens pre-conditioned to different RH.
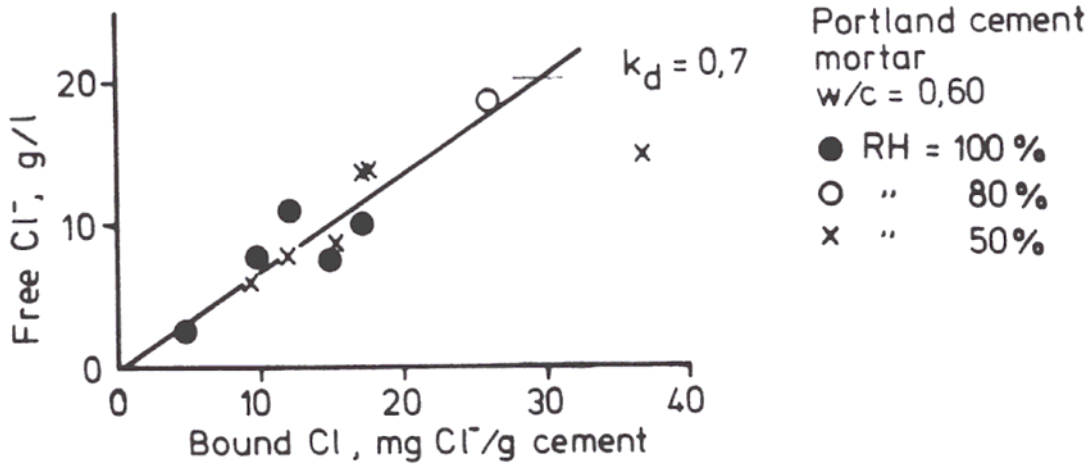
Figure 3: Relation between free (c´´) and bound (c$_b$´´) chloride. w/c 0.6. Tuutti (1982).

In the figures above, *free* chloride c´´ is expressed in the unit *gram per litre pore water*. But c´´ (g/litre) = c (kg/m^3).

Bound chloride c$_b$´´ is in the figures expressed in the unit *mg per g cement*. The total bound chloride in 1 m^3 of concrete, c$_b$´ (kg per m^3 concrete) is:

$$c_b´=c_b´´·10^{-3}·C \tag{9}$$

Where C is the cement content (kg per m^3 concrete). The total pore water volume in 1 m^3 of saturated OPC concrete W$_p$ (m^3 pore water per m^3 concrete) is:

$$W_p=C(W/C-0.19α)/1000 \tag{10}$$

Where α is the degree of hydration and 1000 is the density of water (kg/m^3). Thus, the amount of chloride extracted from the pore water by adsorption or chemical binding, c$_b$ (kg chloride per m^3 pore water), to be used in equation (4) is *(provided all pore water is able to dissolve chloride to the same extent, i.e. that all pore water is active in chloride transport)*:

$$c_b=c_b´/W_p=c_b´·1000/(W/C-0.19α) \tag{11}$$

The coefficient R in equation (3) and (4) becomes:

$$R=c_b/c=(c_b´´/c)/(W/C-0.19α) \tag{12}$$

Since binding is linear the value of R is independent of the total amount of chloride. The following examples give the value of R for the materials in Figure 2 and 3.

> ***Example 3****: Figure 2: W/C=0.40, α=0.6:*
> c≈20 g/l=20kg/m^3 when c$_b$´´=30 mg/g cement.
>
> R=(30/20)/(0.4-0.19·0.6)=**5.2**

As said above, these values are based on analysis of pore water forced out of the concrete by so-called pore pressing. The higher relative value of bound chloride in the specimen with w/c-ratio 0.40 might to a certain extent depend on that it was not possible to "squeeze out" all free water in this dense cement paste. A higher chloride binding in concrete with lower w/c-ratio is not unexpected, however, since the amount of hydration products is higher while the amount of pore water is smaller; see examples 6,8 and 9 below.

The cement in Figures 2 and 3 has the following composition of components influencing chloride binding.

- C_3A: 8 %
- C_4AF: 7 %
- Na_2Oeq: 1.1 %
- Limestone filler: 5 %

3.3 Non-linear relations

As said above, some researchers have found a non-linear relation between free and bound chloride. Examples are given in Figure 4 and 5.

A: Chloride binding as function of the amount of cement gel; Figure 4

An example of *non-linear* chloride binding is shown in Figure 4; Tang & Nilsson (1993). The cement is almost the same as in Figure 2 and 3. The bound chloride is expressed in terms of *mg per g cement gel,* and the free chloride in terms of *concentration in pore water*. The chloride binding curve, expressed in these units, turns out to be independent of the water-cement ratio, which is very reasonable since it is only cement gel (hydration products) that is capable of binding chloride physically and chemically; i.e. the higher the amount of cement gel, the higher is the capacity to bind chloride.
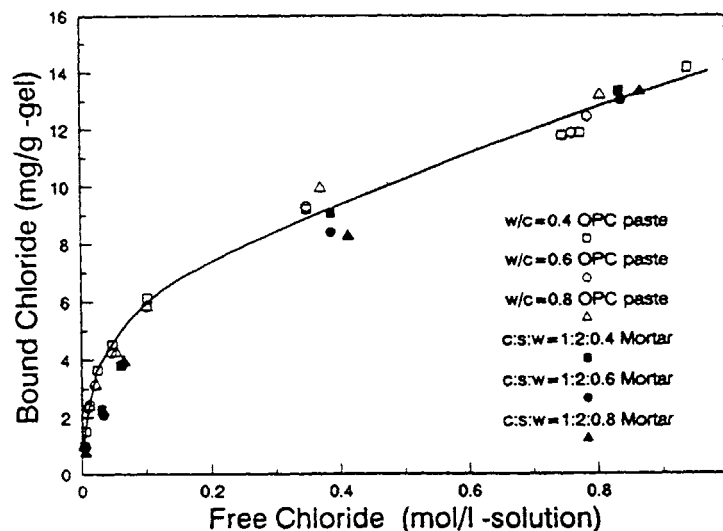

Figure 4: Relation between free and bound chloride; Tang & Nilsson (1993).

The weight of cement gel, Q_{gel} (kg per m^3 concrete, mortar or cement paste) in OPC concrete is:

$$\mathbf{Q_{gel}=1.25 \cdot \alpha \cdot C} \tag{13}$$

Where α is the degree of hydration, and C is the cement content (kg per m^3 concrete).

> *Note:* This equation assumes that all hydration products are included in the "gel", also products created by C_3A and C_4AF. Moreover, calcium hydroxide formed is included in the concept "gel". Thus, weight of "gel" is the same as weight of all hydration products. It must also be observed that the equation (13) is only supposed to be valid for OPC. Other cements, or addition of limestone filler, might change the amount of hydration products.

The higher the amount of free chloride the lower is the fraction of bound chloride. The relation between free and bound chloride is illustrated by some examples. In all examples it is assumed that *all pore water dissolves chloride to the same extent*. Furthermore, it is assumed that all pore water (also gel water) acts as transport medium for chloride diffusion. If not, the fraction of bound chloride will be increased and so will the value of R; see paragraph 5.2.

Examples 5-7: w/c=0.4 (α=0.6)

Example 5
Bound chloride: 6 mg/g cement gel
Weight of cement gel: $Q_{gel}=1.25 \cdot 0.6 \cdot C=0.75C$ kg/m^3 cement paste
Thus, bound chloride is $6 \cdot 10^{-3} \cdot 0.75C=4.5 \cdot 10^{-3}C$ kg bound chloride per m^3 cement paste
The pore water volume is $W_p=C(0.4-0.19 \cdot 0.6)/1000$ m^3 per m^3 cement paste$=2.86 \cdot 10^{-4}C$ m^3/m^3 cement paste
Thus, bound chloride is $c_b=4.5 \cdot 10^{-3}C/2.86 \cdot 10^{-4}C=15.7$ kg per m^3 pore water
Free chloride is 0.1 mole/l $=c=3.55$ kg per m^3 pore water

The relation between bound and free chloride is **R=c_b/c=15.7/3.55=4.4**

Example 6
Bound chloride: 10 mg/g cement gel
Weight of cement gel is the same as in Example 5; 0.75C kg/m^3 cement paste
Thus, bound chloride is $10 \cdot 10^{-3} \cdot 0.75C=7.5 \cdot 10^{-3}C$ kg bound chloride
per m^3 cement paste
The pore water volume is the same as in Example 5; $2.86 \cdot 10^{-4}C$ m^3/m^3 paste
Thus, bound chloride is $c_b=7.5 \cdot 10^{-3}C/2.86 \cdot 10^{-4}C=26.2$ kg per m^3 pore water
Free chloride is 0.5 mole/l $= c=17.8$ kg per m^3 pore water

The relation between bound and free chloride is **R=c_b/c=26.2/17.8=1.5**

Example 8: w/c=0.6 (α=0.75)

Example 8
Bound chloride: 10 mg/g cement gel
The weight of cement gel is, $Q_{gel} = 1.25 \cdot 0.75 \cdot C = 0.94C$ kg/m^3 cement paste
Thus, bound chloride is $10 \cdot 10^{-3} \cdot 0.94C = 9.4 \cdot 10^{-3}C$ kg bound chloride
per m^3 cement paste
The pore water volume is $W_p = C(0.6 - 0.19 \cdot 0.75)/1000$ m^3 per m^3 cement
paste$=4.58 \cdot 10^{-4}C$ m^3/m^3 cement paste
Thus, bound chloride is $9.4 \cdot 10^{-3}C/4.58 \cdot 10^{-4}C = c_b = 20.5$ kg per m^3 pore water
Free chloride is 0.5 mole/l =c=17.8 kg per m^3 pore water

The relation between bound and free chloride is **R=c_b/c=20.5/17.8=1.2**

Example 9: w/c=0.8 (α=0.8)

Example 9
Bound chloride: 10 mg/g cement gel
The weight of cement gel is, $Q_{gel} = 1.25 \cdot 0.8 \cdot C = 1.0C$ kg/m^3 cement paste
Thus, bound chloride is $10 \cdot 10^{-3} \cdot 1.0C = 10 \cdot 10^{-3}C$ kg bound chloride
per m^3 cement paste
The pore water volume is $W_p = C(0.8 - 0.19 \cdot 0.8)/1000$ m^3 per m^3 cement
paste$=6.48 \cdot 10^{-4}C$ m^3/m^3 cement paste
Thus, bound chloride is $10 \cdot 10^{-3}C/6.48 \cdot 10^{-4}C = c_b = 15.4$ kg per m^3 pore water
Free chloride is 0.5 mole/l = c=17.8 kg per m^3 pore water

The relation between bound and free chloride is **R=c_b/c=15.4/17.8=0.9**

A comparison between Examples 8, 9 and 6 shows that the relation between free and bound chloride, as defined by the coefficient R, depends on the water-cement ratio. The reason is that the amount of pore water is dependent on the w/c-ratio. A similar effect of water-cement ratio was observed in Examples 3 and 4.

B: Chloride binding as function of the alkalinity of the pore water; Figure 5
Figure 5 shows that the amount of bound chloride is reduced when the alkalinity of the pore water is increased by adding extra hydroxide.
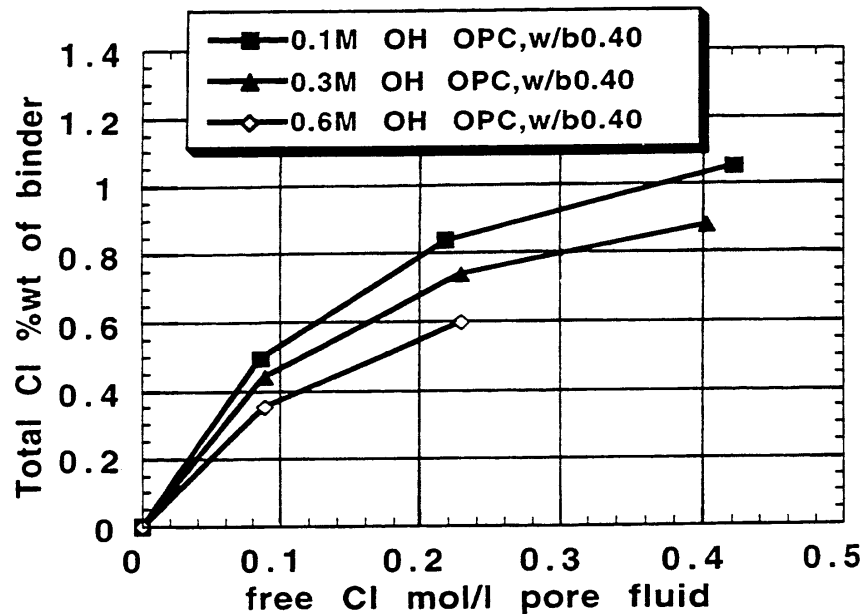

Figure 5: Relation between free and total chloride as function of the OH-ion concentration of the pore water; Sandberg & Larsson (1993). w/c-ratio=0.40.

The relation between free and bound chloride as function of alkalinity and chloride concentration are shown by some examples. The degree of hydration is supposed to be 0.6 in all examples.

Examples 10 - 12; OH-concentration 0.3 mole/litre

> ***Example 10: Total chloride: $0.004 \cdot C$ kg per m^3 concrete.***
> Free chloride is 0.08 mole/l = 2.8 g per litre pore water = c= 2.8 kg
> per m^3 pore water (figure 5).
> The pore water volume is $W_p=C(0.4-0.19\cdot0.6)/1000$ m^3 per m^3 concrete=
> =$2.86\cdot10^{-4}C$ m^3/m^3 concrete
> Thus, the free chloride is $2.8\cdot2.86\cdot10^{-4}C$ kg per m^3 concrete=$8\cdot10^{-4}C$ kg
> per m^3 concrete
> Bound chloride is $0.004C-0.0008C=0.0032C$ kg per m^3 concrete
>
> The relation between bound and free chloride is **R=c_b/c=0.0032/0.0008=4**

Example 11: Total chloride: 0.006·C kg per m³ concrete.
Free chloride is 0.16 mole/l = 5.7 g per litre pore water = 5.7 kg per m³ pore water.
The pore water volume is $2.86 \cdot 10^{-4}C$ m³/m³ concrete (same as Example 10)
Thus, the free chloride is $5.7 \cdot 2.86 \cdot 10^{-4}C$ kg per m³ concrete=$1.6 \cdot 10^{-3}C$ kg per m³ concrete
Bound chloride is 0.006C-0.0016C=0.0044C

The relation between bound and free chloride is **R=c_b/c=0.0044/0.0016=2.8**

Example 12: Total chloride: 0.01·C kg per m³ concrete.
Free chloride is 0.36 mole/l = 12.8 g per litre pore water = 12.8 kg per m³ pore water.
The pore water volume is $2.86 \cdot 10^{-4}C$ m³/m³ concrete (same as Example 10)
Thus, the free chloride is $12.8 \cdot 2.86 \cdot 10^{-4}C$ kg per m³ concrete=$3.7 \cdot 10^{-3}C$ kg per m³ concrete
Bound chloride is 0.008C-0.0037C=0.0043C

The relation between bound and free chloride is **R=c_b/c=0.0043/0.0037=1.2**

Example 13; OH-concentration 0.1 mole/litre

Example 13: Total chloride: 0.006·C kg per m³ concrete.
Free chloride is 0.13 mole/l = 4.6 g per litre pore water = 4.6 kg per m³ pore water.
The pore water volume is $2.86 \cdot 10^{-4}C$ m³/m³ concrete (same as Example 10)
Thus, the free chloride is $4.6 \cdot 2.86 \cdot 10^{-4}C$ kg per m³ concrete=$1.3 \cdot 10^{-3}C$ kg per m³ concrete
Bound chloride is 0.006C-0.0013C=0.0047C

The relation between bound and free chloride is **R=c_b/c=0.0047/0.0013=3.6**

Example 14; OH-concentration 0.6 mole/litre

Example 14: Total chloride: 0.006·C kg per m³ concrete.
Free chloride is 0.24 mole/l = 8.5 g per litre pore water = 8.5 kg per m³ pore water.
The pore water volume is $2.86 \cdot 10^{-4}C$ m³/m³ concrete (same as Example 10)
Thus, the free chloride is $8.5 \cdot 2.86 \cdot 10^{-4}C$ kg per m³ concrete=$2.4 \cdot 10^{-3}C$ kg per m³ concrete
Bound chloride is 0.006C-0.0024C=0.0036C

The relation between bound and free chloride is **R=c_b/c=0.0036/0.0024=1.5**

A comparison between examples 11, 13 and 14 shows that the amount of bound chloride is highly dependent on the alkalinity of the pore water; the higher the alkalinity the lower the fraction of bound chloride.

The fraction of bound chloride, especially at high total chloride content, is considerably lower for the concrete in Figure 5 than for the concretes in Figures 2 and 3.

One reason could be the different composition of the cements used. The cement in Figure 5 has the following composition of components influencing chloride binding.

- C_3A: 1.4 %
- C_4AF: 14 %
- Na_2Oeq: 0.5 %
- Limestone filler: 0 %

Particularly the component C_3A is considerably lower than for the cement in Figure 2, 3 and 4.

3.4 Conclusions concerning binding of chloride

The calculations made above, concerning the relation between bound and free chloride when this is expressed by the coefficient R, show that it is not possible to find any value of R that can be universally applied. See Figure 6 where all data from Examples 3-9 are collected.
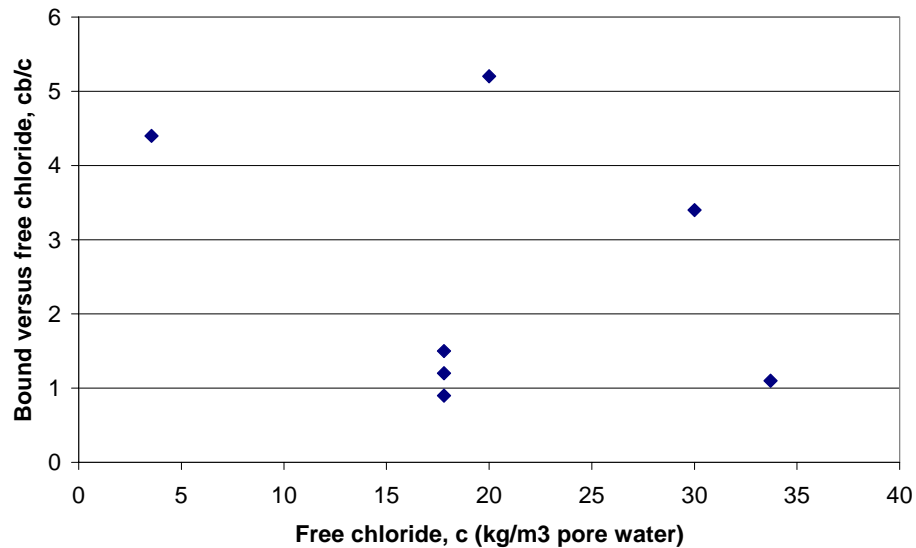

Figure 6: Relation between the free (c) and bound chloride (c_b). Data from Examples 3-9.

The best approach to describe bound chloride seems to be that used in Figure 4 where bound chloride is related to the amount of cement gel (hydration products). It is quite clear, however, that such a relation depends very much on the chemical composition of the cement, especially its contents of aluminates and alkali hydroxide. It is also probable that the use of partly reactive fillers such as limestone will have an effect on the binding capacity.

The examples indicate clearly that the relation between bound and free chloride as defined by coefficient R (kg per m^3 pore solution) is decreased with increased w/c-ratio. This is a direct consequence of the fact that binding is proportional to the amount of hydration products, while the free chloride is proportional to the amount of pore water. A plot of all data for bound chloride versus the w/c-ratio from Examples 3-9 are made in Figure 7.
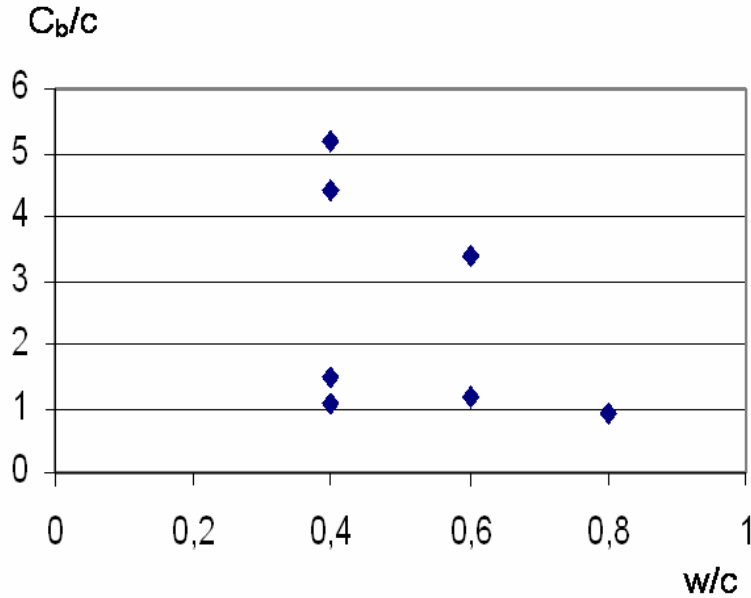

Figure 7: Relation between the free c and bound chloride (c_b) versus the w/c-ratio. Data from Examples 3-9.

The effect of water-cement ratio on chloride binding, and thus on the effective chloride diffusion coefficient, is further discussed in ANNEX 1 and ANNEX 2.

4 Limestone filler in concrete – possible effects on chloride penetration

Alt 1: The filler is completely inert

If a completely inert material is added to a concrete with fixed water-cement ratio there should be *no effect* on the rate of chloride ingress in concrete for the following reasons:

1. The "steady state" diffusion coefficient δ_0 should be unchanged since the inert filler does, by definition of "inert", not create any new hydration products or modification of the ordinary hydration products. Thus, the chloride permeability δ_0 is unchanged.
2. The binding of chloride is unchanged since the filler is supposed to be inert also with regard to chloride. Thus, also the coefficient R in equation (3) is unchanged.
3. This means that the effective diffusion coefficient $\delta_{eff} = \delta_0/(R+1)$ is unaffected by the filler

Alt 2: The filler does not change the pore structure but it reacts with components binding chloride

The main cement components determining the built-up of the pore structure, the calcium silicates C_3S and C_2S, are supposed not to be affected by the filler. Therefore, the pore structure and the permeability are supposed to be unchanged. On the other hand, the filler is supposed to react with components binding chloride, mainly C_3A, and possibly to some extent C_4AF; Bonavetti, Rahal & Irassar (2001)

In this case, the filler might increase the rate of chloride ingress in concrete for the following reasons:
1. The "steady state" diffusion coefficient δ_0 is unchanged since the pore structure is unchanged.
2. The binding capacity for chloride is reduced since the reaction components formed by reaction of C_3A (and C_4AF) with the filler is assumed not to be capable of binding chloride to the same extent as the normal reaction products of C_3A (formation of Friedel´s salt). Reduced binding capacity means that the coefficient R in equation (3) is reduced.
3. Consequently the effective diffusion coefficient $\delta_{eff} = \delta_0/(R+1)$ is increased.

The effect of filler is illustrated by two examples.

> ***Example 15 (based on Figure 2, Example 3)***
> Before addition of filler the value of R is 5.2. The effective diffusion coefficient is assumed to be δ_{eff}=**5·10^{-12} m^2/s.**
> Thus, the steady state diffusion coefficient is δ_0=(5.2+1)5·10^{-12}=31·10^{-12} m^2/s.
>
> After addition of filler the binding capacity is halved; i.e. R=2.6. The effective diffusion coefficient becomes
> δ_{eff}=**31·10^{-12}/(2.6+1)=8.6·10^{-12} m^2/s**

Example 16 (Based on Figure 4, Example 6)
Before addition of filler the value of R is 1.5. The effective diffusion coefficient is assumed to be $\delta_{eff}=5\cdot10^{-12}$ m^2/s.
The steady state diffusion coefficient is $\delta_0=(1.5+1)5\cdot10^{-12}=12.5\cdot10^{-12}$ m^2/s.

After addition of filler the binding capacity is halved; i.e. R=0.8. The effective diffusion coefficient becomes
$\delta_{eff}=12.5\cdot10^{-12}/(0.8+1)=$**6.9$\cdot$10^{-12} m^2/s**

According to these examples the filler reaction has increased the diffusion coefficient by 72% (Example 15) or 38 % (Example 16) despite the fact that the w/c-ratio is unchanged. This shows that limestone-filler might have a detrimental effect. This can also be expressed in terms of limestone filler having a *"negative efficiency factor with regard to chloride ingress"*; i.e. each kilo of limestone filler added to the concrete requires increased cement content if the ingress of chloride shall not increase.

Alt 3: The filler reacts with components binding chloride and also modifies the pore structure
As in Alt 2 the filler is supposed to react with components binding chloride, mainly C_3A, and to some extent C_4AF, reducing their capacity for binding chloride. Furthermore, the pore structure is supposed to be changed by this reaction. In this case the filler might increase the rate of chloride ingress in concrete for the following reasons:

1. The "steady state" diffusion coefficient δ_0 is increased since the pore structure is changed in a way that gives an increased permeability. The new steady state diffusivity is $(1+\Delta)\delta_0$ where Δ is the increase in diffusivity. (In reality there will probably be a reduced value of δ_0).
2. The binding capacity for chloride is reduced by the same mechanism as in Alt 2. Reduced binding capacity means that the coefficient R in equation (3) is reduced.
3. Consequently, the effective diffusion coefficient $\delta_{eff}=\delta_0/(R+1)$ is increased.

Example 17 (based on Figure 2, Example 3)
Before addition of filler the value of R is 5.2. The effective diffusion coefficient is assumed to be $\delta_{eff}=5\cdot10^{-12}$ m^2/s.
Thus, the steady state diffusion coefficient is $\delta_0=(5.2+1)5\cdot10^{-12}=31\cdot10^{-12}$ m^2/s.

After addition of filler the steady state diffusion coefficient is increased by 25%; i.e $\delta_0=1.25\cdot31\cdot10^{-12}=3.9\cdot10^{-11}$m2/s. The binding capacity is halved; i.e. R=2.6.
The effective diffusion coefficient becomes
$\delta_{eff}=3.9\cdot10^{-11}/(2.6+1)=$**10.8$\cdot$10^{-12} m^2/s**

The diffusion coefficient is increased by 116% by the addition of filler.

5 Experimental methods for determination of the effect of limestone filler on chloride diffusion and binding

5.1 Introduction

In order to investigate the effect of limestone filler on chloride penetration in concrete its effects on chloride diffusivity and chloride binding should be determined. This will elucidate the theoretical background to the observations made that limestone filler might have a negative "efficiency factor" with regard to chloride penetration.

The measurements should preferably be made on cement pastes or mortars with different fixed w/c-ratio. Thus, the filler should be used as *addition* and not as replacement of cement.

5.2 The "steady state" diffusion coefficient

The steady state diffusion coefficient reveals the effect of filler on the chloride permeability of the cement paste. If the filler is not inert, but reacts with the cement, one might suspect that the permeability is reduced, so that also the diffusion coefficient δ_0 is reduced.

A diffusion cell of the type shown in Figure 8 could be used. The solution in the two chambers should be an artificial pore solution in order to avoid leaching of OH⁻ and lime from the mortar. One way of creating such a solution is to mix a cement paste or cement mortar with the actual composition, and after some time -just before the cement binds- extract the water in the paste or mortar by vacuum. The mix is poured in a funnel with filter paper placed in a vacuum flask. The technique is described in Fagerlund (1982).

The steady state diffusion coefficient can be identified by continuous measurements of the change in the Cl-concentrations in the two chambers.
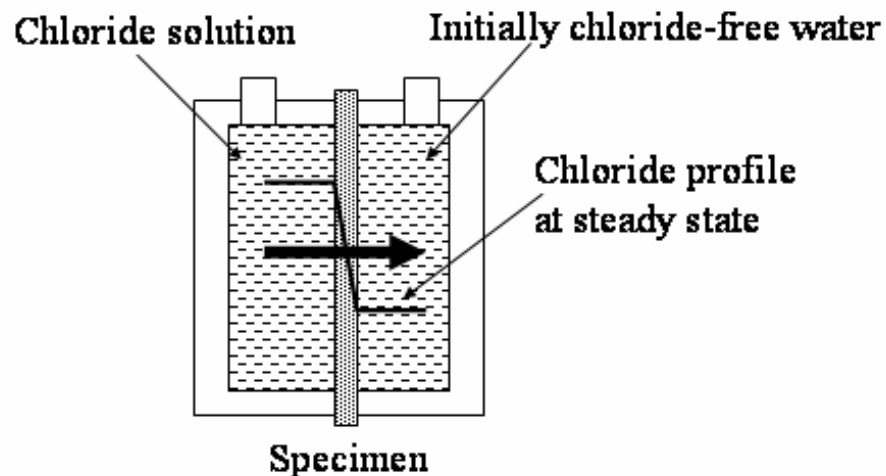

Figure 8: Diffusion cell for determination of the (steady-state) diffusion coefficient, δ_0

Measurements are made for mortar with different w/c-ratio and different amount of limestone filler of different quality. Comparisons are made with normal mortar without filler.

The evaluation technique is described in ANNEX 3.

5.3 Chloride binding

Bound chloride is the difference between total and free chloride:

$$c_b' = c_{tot}' - c' \qquad (14)$$

where c_b', c_{tot}' and c' are the bound chloride, the total chloride and the free chloride respectively, all expressed in the unit kg per m^3 of dry material.

A thin slice of the material (cement paste or mortar) is immersed in a solution with known chloride concentration. The base-solution should preferably be as like the pore solution as possible in order to avoid leaching from the specimen; see above.
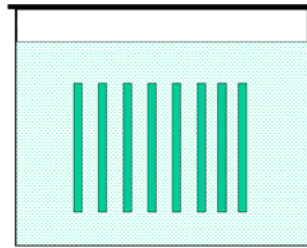
Figure 9: Long-term storage of thin slices in chloride solution of known concentration, c
kg/m³.

After long time, there is equilibrium between the chloride concentration in the pores and the concentration of the outer solution. Then, the specimen is taken up, pulverised and dissolved in an acid that dissolves all chloride. The total chloride content c_{tot}' is determined by titration.

From the known pore volume the amount of dissolved chloride c' is calculated. The free chloride content becomes:

$$c' = c \cdot W_w \qquad (15)$$

Where W_w is the amount of pore water able to dissolve chloride (m^3 per m^3 of concrete), c is the chloride concentration in the bath (kg per m^3).

It is, as a first approximation, assumed that all evaporable pore water is capable of dissolving chloride; i.e.:

$$c' = c \cdot C(W/C - 0.19 \cdot \alpha)/1000 \qquad (16)$$

Where C is the cement content (kg per m^3 of concrete), α is the degree of hydration, and 1000 is the density of water (kg/m^3).

Possibly, the "gel-water" is not dissolving chloride to the same extent as the capillary water, and, therefore, not taking part in chloride transport. If this is the case, the bound chloride and the value of R will be higher as shown by the examples below.

The bound chloride c_b' can be calculated by equation (14). The chloride binding curves in Figures 3 and 4 were determined by this type of technique.

These examples show that it is extremely important to use the correct pore volume in the calculation of free chloride.

According to Figure 4 the chloride binding is proportional to the amount of cement gel. This means that one might obtain a more correct relation between free and bound chloride by using concrete with low amount of gel pores; i.e. with material with high w/c-ratio. This is shown by the following examples.

The difference between the two different ways of defining the pore volume that is able to dissolve chloride is now much smaller than when concrete with low w/c-ratio was used.

The true water volume that is able to dissolve chloride W_w (m^3 per m^3 concrete) is:

$$W_w = C(W/C-\gamma\cdot\alpha)/1000 \qquad (17)$$

Where $0.19 \leq \gamma \leq 0.39$.

In ANNEX 4 an experimental method for determination of the "active" porosity, i.e. the coefficient γ, is outlined.

Instead of calculating the total pore volume, as is made in the examples above, one can determine it experimentally. The total pore volume is determined in the traditional way using vacuum saturation and weighing in air and water, subtracting air-pores and compaction pores, which are supposed not to take up water. The capillary pore volume can be approximately calculated as the difference between the water content at complete saturation (coarse air-pores and similar pores excluded) and the water content at equilibrium with about 45% RH.

Measurements of chloride binding by the method described shall be made for many different chloride concentrations and for mortar with different w/c-ratio and different amount of limestone filler of different quality. Comparisons are made with normal mortar without filler.

The time needed for establishing equilibrium with the outer solution depends on the thickness of the specimen, and on its chloride diffusivity. The time needed t (s) is given by the Fourier number Fo:

$$Fo = 4 \cdot \delta_{eff} \cdot t / L^2 \tag{18}$$

where L is the specimen thickness (m). Equilibrium is almost reached when Fo=1.5; Crank (1985). This corresponds to the time:

$$t = 1.5 \cdot L^2 / (4 \cdot \delta_{eff}) \tag{18'}$$

The lowest possible value of δ_{eff} is about $5 \cdot 10^{-13}$ m^2/s. For a specimen thickness 5 mm the time needed is then:

$$t = 1.5 \cdot (5 \cdot 10^{-3})^2 / (4 \cdot 5 \cdot 10^{-13}) = 1.9 \cdot 10^7 \text{ s} = 217 \text{ days}$$

For concrete of normal quality the time needed is shorter.

6. Conclusions

Chloride ingress in concrete is a very complicated process. Above all, the binding of chloride by adsorption and chemical reaction is not very well understood. Some data from literature on chloride binding are reviewed. A promising approach is that exemplified in Figure 4; i.e. assuming that binding is proportional to the amount of hydration products. These can, as a first approximation, be described by equation (13), although this is only valid for OPC without addition of reactive material.

The use of limestone filler in concrete might have an impact on the rate by which chloride is entering the concrete. It might affect both the steady state chloride permeability by changing the pore structure, and change the chloride binding capacity by reacting with aluminates in the concrete. These effects ought to be investigated experimentally. Test methods are suggested.

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ANNEX 1

CHLORIDE BINDING AS FUNCTION OF THE WATER-CEMENT RATIO AND AGE

A1.1 Theory

In this ANNEX an attempt is made to find a relation between the coefficient R describing chloride binding -see equation (3)- and the composition and age of the concrete.

It is assumed that chloride binding is directly proportional to the amount of cement gel; see Figure 4 and equation (15).The amount of bound chloride is:

$$c_b' = c_{b,gel} \cdot 1.25 \cdot \alpha \cdot C \tag{A1}$$

Where c_b' is the amount of bound chloride in unit volume of concrete (kg per m^3 concrete), $c_{b,gel}$ is the amount of bound chloride in unit weight of gel (kg chloride per kg cement gel), $1.25 \cdot \alpha \cdot C$ is the amount of gel in unit volume of concrete (kg gel per m^3 concrete), α is the degree of hydration, C is the cement content (kg cement per m^3 concrete). Instead of considering a unit volume of concrete a unit volume of cement mortar or cement paste can be considered. It will not alter the equation.

The coefficient $c_{b,gel}$ will depend on the chloride concentration of the pore solution as shown in Figure 4.

The amount of bound chloride will depend on the fraction of pore water dissolving chloride, and therefore participating in the chloride transport process, "delivering" chloride to be bound during the transport. Two possibilities are investigated:

- Alt A. All pore water participates.
- Alt B. only capillary pore water participates.

Alt A: All pore water is assumed to dissolve chloride and therefore also assumed to take part in chloride transport

The volume of pore water dissolving chloride is (provided the concrete is saturated and the aggregate is non-porous):

$$W_w = C(W/C - 0.19 \cdot \alpha)/10^3 \tag{A2}$$

Where W_w is the volume of pore water in unit volume of concrete (m^3 pore water per m^3 of concrete).

The amount of bound chloride extracted from the pore solution during diffusion therefore is:

$$c_b = c_b'/W_w = c_{b,gel} \cdot 1.25 \cdot \alpha \cdot 10^3/(W/C - 0.19 \cdot \alpha) \tag{A3}$$

Where c_b is the amount of extracted chloride by binding (kg bound chloride per m^3 pore solution).

The free chloride concentration in the pore water is c (kg chloride per m³ pore water). Thus, the coefficient R as defined by equation (3) becomes:

$$R = c_b/c = (c_{b,gel}/c) \cdot 1.25 \cdot \alpha \cdot 10^3/(W/C - 0.19 \cdot \alpha) \qquad \text{(A4)}$$

Where $c_{b,gel}/c$ is given by the chloride binding isotherm (e.g. Figure 4).

For *75% degree of hydration* equation (A4) becomes:

$$R = (c_{b,gel}/c) \cdot 0.94 \cdot 10^3/(W/C - 0.14) \qquad \text{(A4´)}$$

Thus, for a given chloride concentration of pore water, the coefficient R is only a function of the water-cement ratio. Furthermore, the lower the w/c-ratio the bigger the value of R.

Alt B: Only capillary pore water is assumed to dissolve chloride and therefore also assumed to take part in chloride transport

The volume of pore water dissolving chloride (m³ per m³ of concrete) is:

$$V_w = C(W/C - 0.39 \cdot \alpha)/10^3 \qquad \text{(A5)}$$

The amount of bound chloride extracted from the pore solution during diffusion therefore is:

$$c_b = c_b´/V_w = c_{b,gel} \cdot 1.25 \cdot \alpha \cdot 10^3/(W/C - 0.39 \cdot \alpha) \qquad \text{(A6)}$$

Thus, the coefficient R as defined by equation (3) becomes:

$$R = c_b/c = (c_{b,gel}/c) \cdot 1.25 \cdot \alpha \cdot 10^3/(W/C - 0.39 \cdot \alpha) \qquad \text{(A7)}$$

For *75% degree of hydration* equation (A4) becomes:

$$R = (c_{b,gel}/c) \cdot 0.94 \cdot 10^3/(W/C - 0.29) \qquad \text{(A7´)}$$

A1.2 Results

Some examples of equations (A4´) and (A7´) showing the effect of w/c-ratio on the coefficient R are given in Table A1. The data for c and $c_{b,gel}$ are taken from Figure 4.

Table A1: The coefficient R based on the chloride binding curve in Figure 4.
Degree of hydration 0.75.

Free chloride c		Bound chloride	R equation (A4´)			R equation (A7´)		
mole/litre	kg/m³	$c_{b,gel}$ (kg/kg)	w/c 0.4	w/c 0.5	w/c 0.6	w/c 0.4	w/c 0.5	w/c 0.6
0.2	7.1	$7 \cdot 10^{-3}$	3.6	2.6	2.0	8.4	4.4	3.0
0.4	14.2	$9 \cdot 10^{-3}$	2.3	1.7	1.3	5.4	2.8	1.9
0.8	28.4	$13 \cdot 10^{-3}$	1.7	1.2	0.9	3.9	2.0	1.4

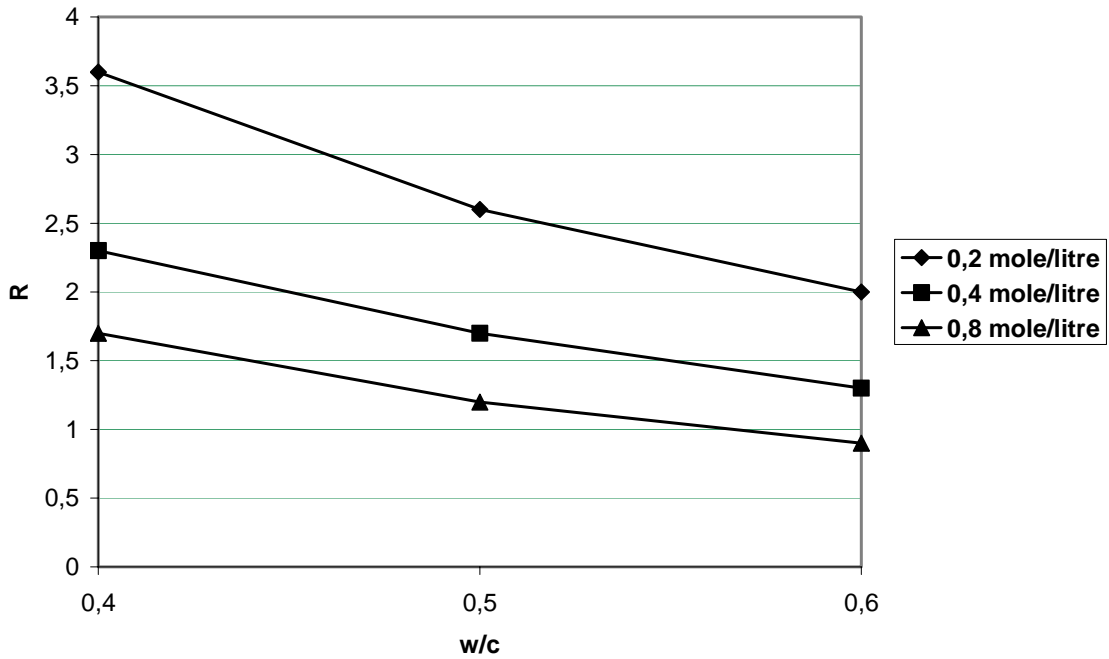The data in Table A1 are also plotted in Figure A1, A2 and A3.

Figure A1. Effect of w/c-ratio on the coefficient R. Data from Table A1.
All pore water participates in chloride transport; equation (A4).Degree of hydration 0.75.
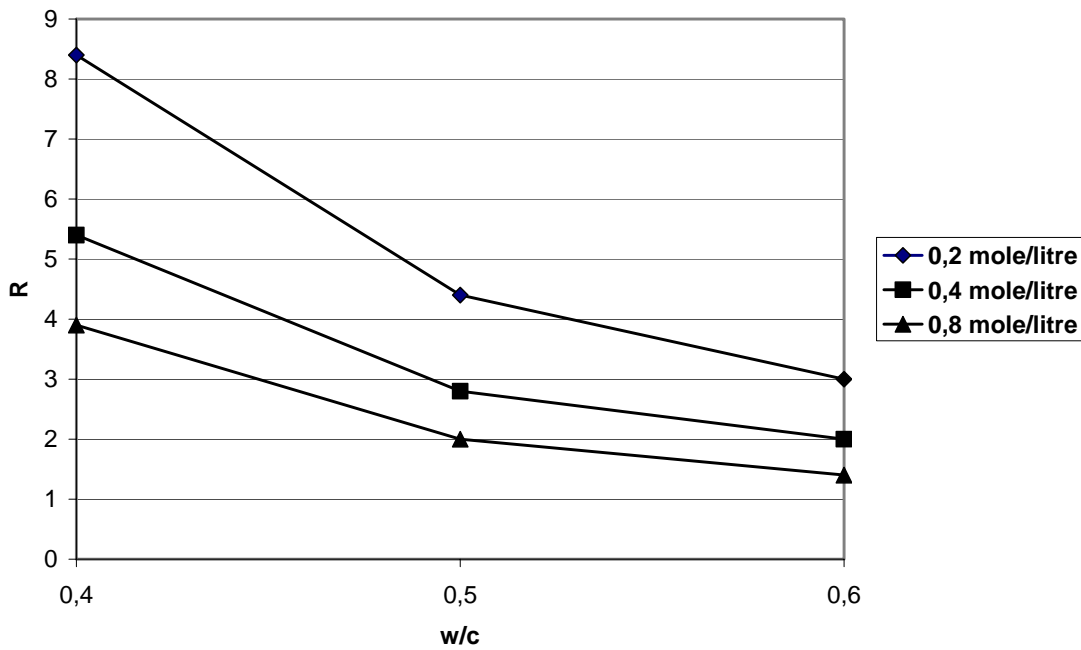

Figure A2. Effect of w/c-ratio on the coefficient R. Data from Table A1.
Only capillary pore water participates in chloride transport; equation (A7).
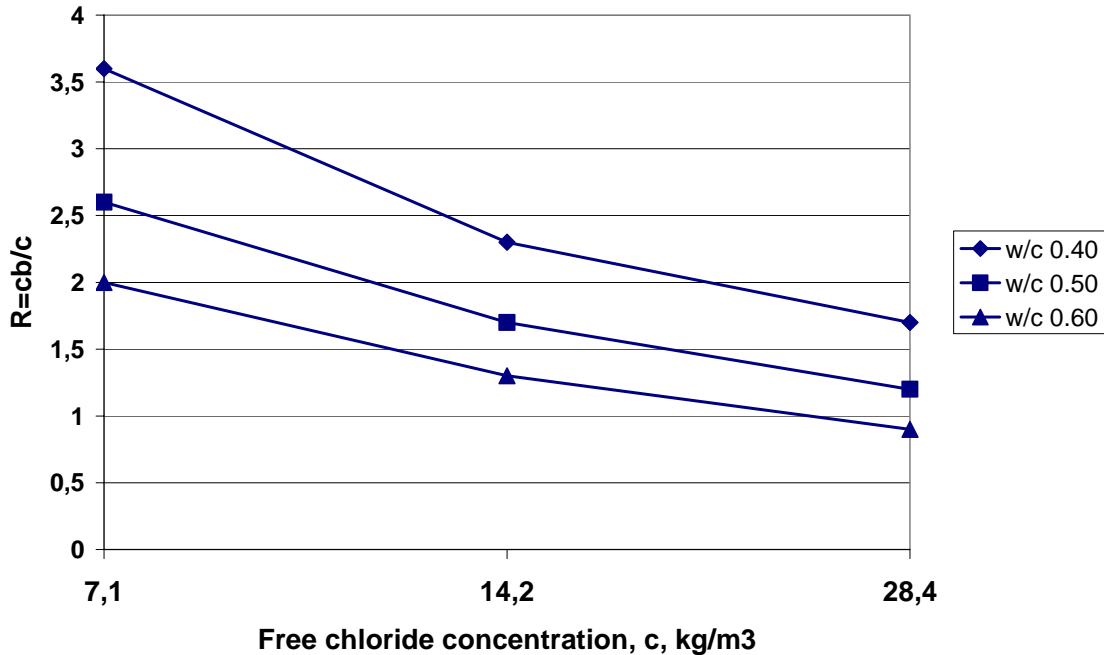*Degree of hydration 0.75.*

Figure A3. Effect of the free chloride concentration on the coefficient R. Data from Table A1. All pore water participates in chloride transport; equation (A4). Degree of hydration 0.75.

The analysis shows that the chloride binding is bigger, and therefore has a larger retarding effect on the chloride transport, the lower the w/c-ratio is.

It is also shown that the difference between different ways of defining volume of pore solution is very big for low free concentration and low w/c-ratio.

Furthermore, chloride binding has bigger effect the higher the degree of hydration is. This is illustrated by Example A1.

Example A1: Data from Figure 4; c=14.2 kg/m³, c_{b,gel}=9·10^{-3} kg/kg
   W/C =0.50

	Equation (A4)	*Equation (A7)*
α =0.25	R =0.44	R =0.49
α =0.50	R =0.98	R =1.30
α =0.75	R =1.66	R =2.86
α =1.0	R =2.56	R =7.20

More examples on the effect of degree of hydration on chloride binding are given in Figure A4.
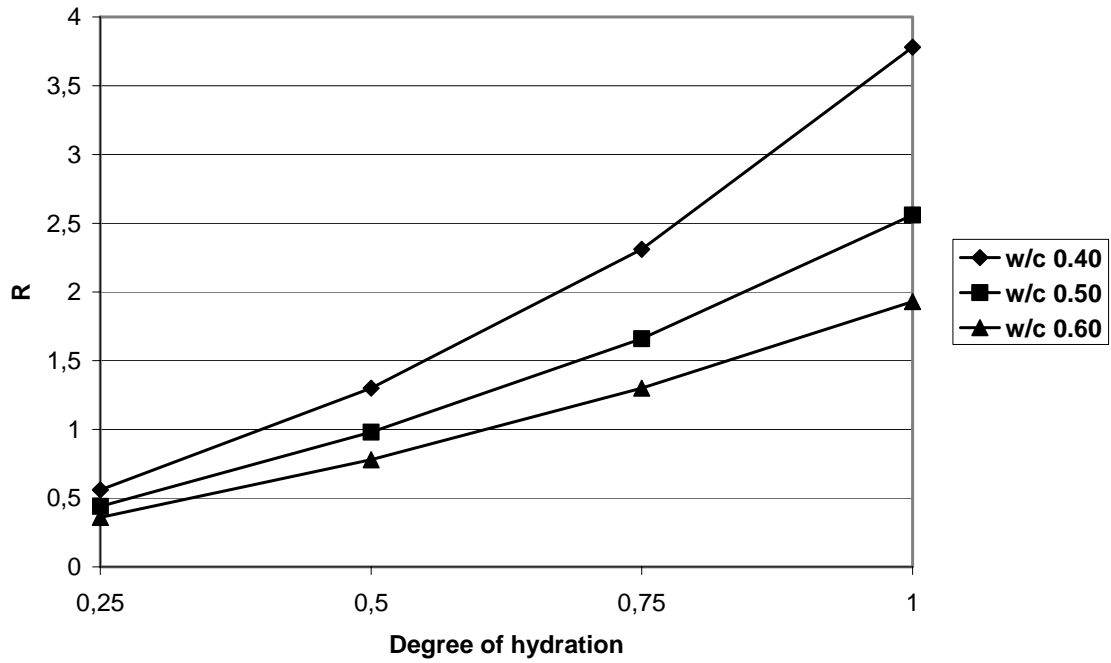
30

Figure A4. Effect of the degree of hydration on the coefficient R. Data from Figure 4.
*Calculations based on equation (A4).*

A1.3 Imaginable effect of limestone filler

As described in paragraph 4, limestone filler might change *chloride binding* by changing the parameter $c_{b,gel}$. Thus, Figure 4 can hardly be applied also to concrete with limestone filler. New interrelated values between the free concentration c and the bound chloride $c_{b,gel}$ must be determined, e.g. by the technique described in paragraph 5.3. The hypothetical effect of limestone filler on the "chloride binding isotherm" is shown in Figure A5. In the figure it is assumed that the hydration products (the "gel") bind less chloride in concrete with limestone filler.

It is assumed that the pore water volumes described by equations (A2) and (A5) are valid also for concrete with limestone filler. Principally, this hypothesis should be tested by comparative measurements of porosity and water sorption isotherms on cement paste (or mortar) with and without filler.

This means that equations (A4) and (A7) can also be used for concrete with limestone filler but with other values of $c_{b,gel}$.

Bound chloride in cement gel, $c_{b,gel}$ (kg/kg)

Without filler

With filler
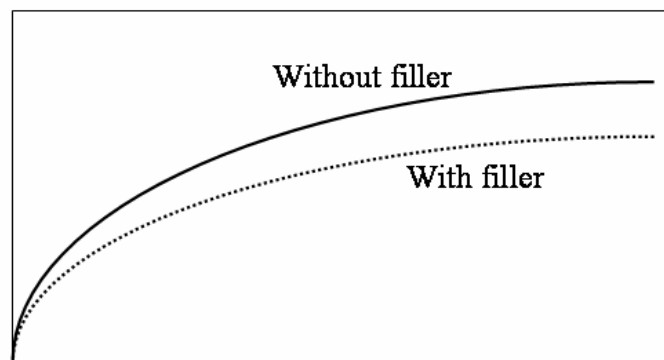
Free chloride, c (kg/m³)

Figure A5: Effect of limestone filler on chloride binding. Hypothetic relations.

ANNEX 2

EFFECTIVE CHLORIDE DIFFUSION COEFFICIENT AS FUNCTION OF THE WATER-CEMENT RATIO AND AGE

A2.1 The *relative* effective diffusion coefficient

The relative effective diffusion coefficient is -see equation (5):

$$\delta_{eff}/\delta_0 = 1/(R+1) \tag{A8}$$

Where δ_0 is the "steady state" diffusion coefficient.

Inserting equations (A4) and (A7) in equation (A8) gives:

Alt A: All pore water takes part in chloride transport -equation (A4):

$$\delta_{eff}/\delta_0 = 1/\{[(c_{b,gel}/c)\cdot1.25\cdot\alpha\cdot10^3]/[W/C-0.19\alpha] +1\} \tag{A9}$$

Alt B: Only capillary pore water takes part in chloride transport – equation (A7)

$$\delta_{eff}/\delta_0 = 1/\{[(c_{b,gel}/c)\cdot1.25\cdot\alpha\cdot10^3]/[W/C-0.39\alpha] +1\} \tag{A10}$$

Table A2 shows the calculated effective diffusivity for concrete with 75% degree of hydration. Data for the coefficient R are taken from Table A1.

*Table A2: The **relative** effective chloride diffusion coefficient. Data from Table A1. Degree of hydration 0.75.*

Free chloride	δ_{eff}/δ_0 equation (A9)			δ_{eff}/δ_0 equation (A10)		
c mole/litre	w/c 0.4	w/c 0.5	w/c 0.6	w/c 0.4	w/c 0.5	w/c 0.6
0.2	0.22	0.28	0.33	0.11	0.19	0.25
0.4	0.30	0.37	0.43	0.16	0.26	0.34
0.8	0.37	0.45	0.53	0.20	0.33	0.42

The data in Table A2 are plotted in Figure A6 and A7.

The theoretical analysis shows that there is an almost linear relation between the diffusion coefficient and the w/c-ratio. Such linear relations have also been found experimentally; e.g. Frederiksen et al. (1997).

The reduction in chloride diffusivity caused by binding is bigger the lower the w/c-ratio and the lower the outer concentration of free chloride are.
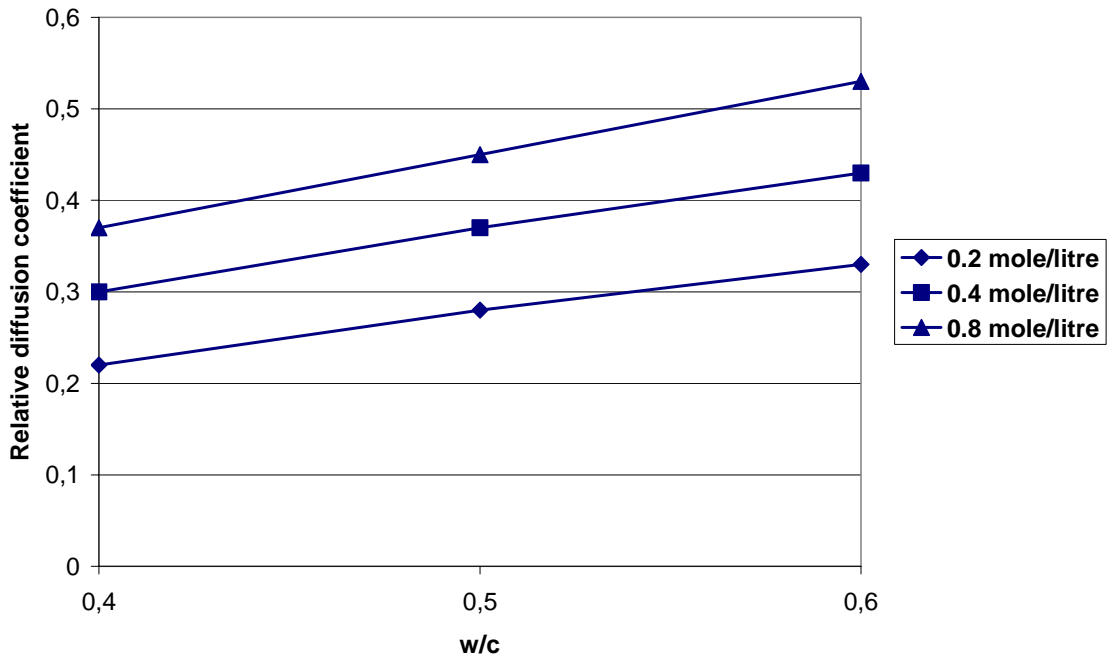
Figure A6: Effect of the w/c-ratio on the relative chloride diffusion coefficient (δ_{eff}/δ_0). Data from Table A2. All pore water participates in chloride transport – equation (A9). Degree of hydration 0.75.
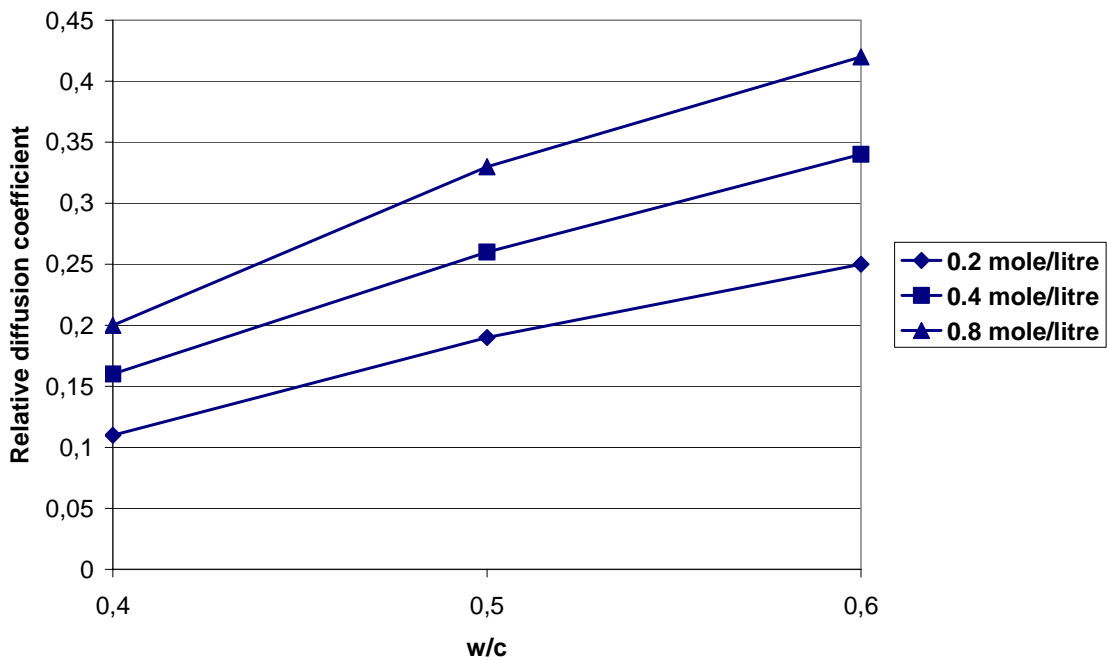

Figure A7: Effect of the w/c-ratio on the relative chloride diffusion coefficient (δ_{eff}/δ_0). Data from Table A2. Only capillary pore water participates in chloride transport – equation (A10). Degree of hydration 0.75.

A consequence of equation (A9) and (A10) is that *the effective diffusion coefficient* is reduced with increased degree of hydration. This is illustrated by Example A2.

Example A2: Values of R taken from Example A1 (W/C 0.50)

$$\delta_{eff}=\delta_0/(R+1)$$

	Equation (A9)	*Equation (A10)*
$\alpha = 0.25$	$\delta_{eff}/\delta_0 = 1/1.44 = 0.69$	$\delta_{eff}/\delta_0 = 1/1.49 = 0.67$
$\alpha = 0.50$	$\delta_{eff}/\delta_0 = 1/1.98 = 0.51$	$\delta_{eff}/\delta_0 = 1/2.30 = 0.43$
$\alpha = 0.75$	$\delta_{eff}/\delta_0 = 1/2.66 = 0.38$	$\delta_{eff}/\delta_0 = 1/3.86 = 0.26$
$\alpha = 1.0$	$\delta_{eff}/\delta_0 = 1/3.56 = 0.28$	$\delta_{eff}/\delta_0 = 1/8.20 = 0.12$

A2.2 The *absolute* effective diffusion coefficient

The steady state diffusion coefficient δ_0 as defined by Equation (2) is valid for the entire concrete surface, which is composed of both solid and porous phases. But chloride is only moving in the porous phase. Thus, the bigger the portion of porous phase the bigger is the value of δ_0. Therefore, δ_0 can, as a first approximation, be assumed to be *directly proportional* to the water-filled porosity, P_w; i.e.:

$$\delta_0 = K \cdot P_w \tag{A11}$$

Where K is a coefficient describing a *fictitious* diffusivity for 100% porosity. K is *independent* of the w/c-ratio.

For a saturated concrete $P_w = P_{tot}$ which is the total porosity; i.e.:

$$\delta_0 = K \cdot P \tag{A11´}$$

Since it is only the cement paste that is porous (neglecting interfaces between stone and cement paste) the porosity in equation (A11´) can be exchanged for the cement paste porosity.

The total porosity of cement paste is:

$$P_{tot} = (W/C - 0.19 \cdot \alpha)/(W/C + 0.32) \tag{A12}$$

The capillary porosity of cement paste is:

$$P_{cap} = (W/C - 0.39 \cdot \alpha)/(W/C + 0.32) \tag{A13}$$

Thus the steady state diffusion coefficient depends on how big part of the porosity that takes part in chloride transport.

Alt A: The total pore volume takes part; i.e.:

$$\delta_0 = K \cdot (W/C - 0.19 \cdot \alpha)/(W/C + 0.32) \tag{A14}$$

The diffusion coefficient δ_{eff} is obtained by inserting equation (A9) and (A14) in (A8):

$$\boldsymbol{\delta_{eff} = K\{(W/C - 0.19\alpha)/(W/C + 0.32)\}/\{[(c_{b,gel}/c)1.25\alpha \cdot 10^3]/[W/C - 0.19\alpha] + 1\}} \tag{A15}$$

Alt B: Only the capillary pore volume takes part; i.e.:

$$\delta_0 = K \cdot (W/C - 0.39 \cdot \alpha)/(W/C + 0.32) \tag{A16}$$

The diffusion coefficient δ_{eff} is obtained by inserting equation (A10) and (A16) in equation (A8):

$$\boldsymbol{\delta_{eff} = K\{(W/C - 0.39\alpha)/(W/C + 0.32)\}/\{[(c_{b,gel}/c)1.25\alpha \cdot 10^3]/[W/C - 0.39\alpha] + 1\}} \tag{A17}$$

The calculated diffusion coefficient for 75% degree of hydration is shown in Table A3.

*Table A3: The **absolute** effective chloride diffusion coefficient. Data from Table A1 and A2. Degree of hydration 0.75.*

Free chloride	δ_{eff} equation (A15)			δ_{eff} equation (A17)		
c mole/litre	w/c 0.4	w/c 0.5	w/c 0.6	w/c 0.4	w/c 0.5	w/c 0.6
0.2	0.080·K	0.123·K	0.165·K	0.0164·K	0.0481·K	0.0836·K
0.4	0.108·K	0.162·K	0.215·K	0.0239·K	0.0658·K	0.114·K
0.8	0.134·K	0.200·K	0.265·K	0.299·K	0.0835·K	0.140·K

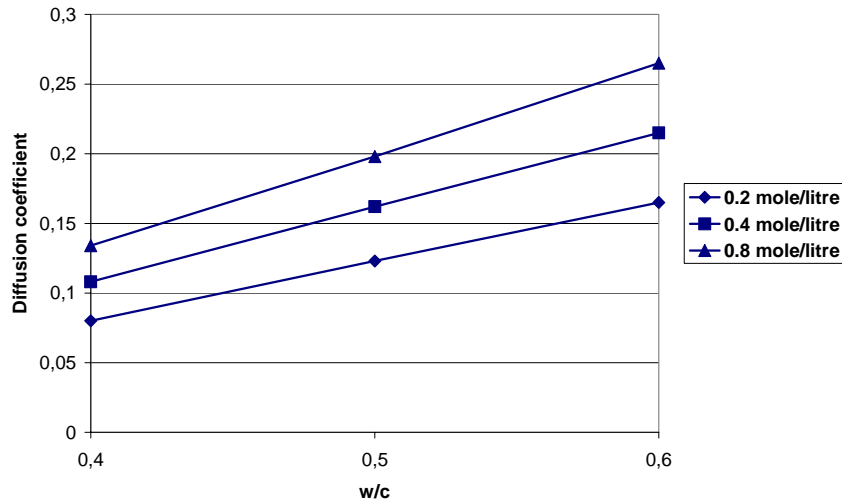Data in Table A3 are also shown in Figures A8, A9 and A10.

Figure A8: The effective diffusion coefficient as function of the w/c-ratio. All pore water takes place in chloride transport; equation (A15). The values shall be multiplied by the coefficient K. Degree of hydration 0.75.
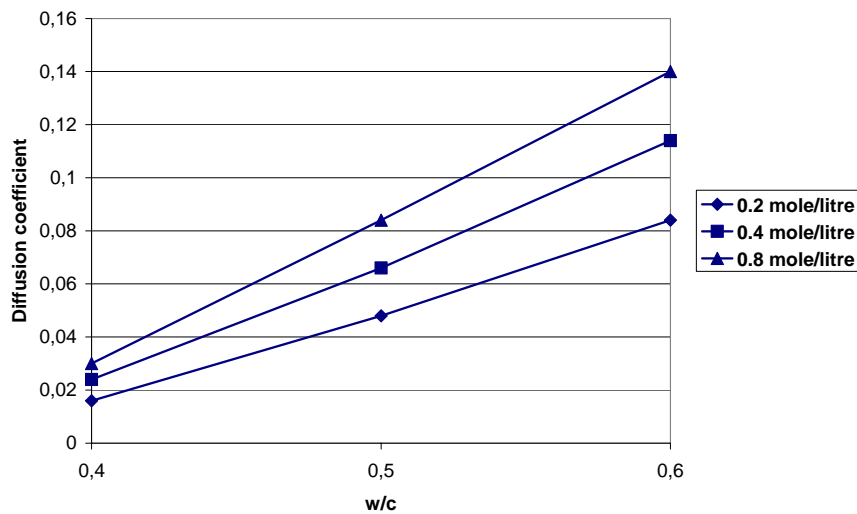

Figure A9: The effective diffusion coefficient as function of the w/c-ratio. Only capillary pore water takes place in chloride transport; equation (A17). The values shall be multiplied by the coefficient K. Degree of hydration 0.75.
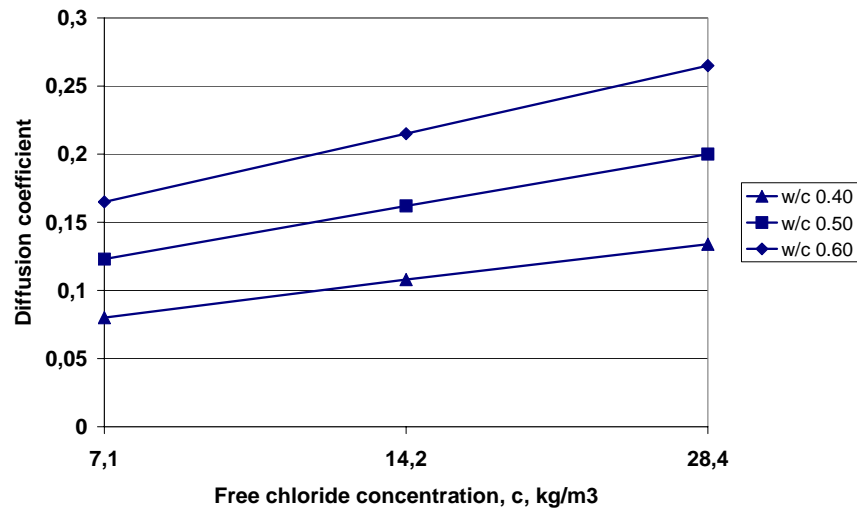
Figure A10: The effective diffusion coefficient as function of the concentration of free chloride. All pore water takes place in chloride transport; equation (A15). The values shall be multiplied by the coefficient K. Degree of hydration 0.75.

The coefficient K should be the same for all w/c-ratios and all degrees of hydration. A value of K can be calculated from known effective diffusion coefficients of concrete. For mature concrete with w/c 0.40 the effective diffusion coefficient in sea water is about $5 \cdot 10^{-12}$ m^2/s. The chloride concentration is about 0.5 mole/litre. Thus, from Table A3 δ_{eff} is about $0.11 \cdot K$ or $0.024 \cdot K$.

This gives the following values of K :

Alt 1: All pore water takes part in chloride transport:

$$K = 5 \cdot 10^{-12} / 0.11 = \mathbf{4.5 \cdot 10^{-11} \ m^2/s}$$

Alt 2: Only capillary pore water takes part in chloride transport:

$$K = 5 \cdot 10^{-12} / 0.024 = \mathbf{2 \cdot 10^{-10} \ m^2/s}$$

The diffusivity of an ion in bulk water is normally of the order 10^{-9} m^2/s. The value of K is only 5% and 20% of that value. This discrepancy can, at least partly, be explained by the "tortuosity effect", i.e. the fact that the ions do not move in straight paths, but have to move in a meandering path inside the pore system.

Using the values of K above, the effect of degree of hydration and w/c-ratio can be calculated by equations (A15) or (A17). This is shown by some examples.

Example A3: Effect of the w/c-ratio on the diffusion coefficient

Assumptions
- Degree of hydration 0.75
- Outer chloride concentration c=0.4 mole/litre. Gives $c_{b,gel}/c = 9 \cdot 10^{-3}/14.2 = 6.3 \cdot 10^{-4}$ (Figure 4, Table A1)
- $K = 4.5 \cdot 10^{-11}$ m^2/s

Equations (A15) and (A17) are applied:

$\delta_{eff} = 4.5 \cdot 10^{-11} \cdot \{(w/c-0.14)/(w/c+0.32)\}/\{[6.3 \cdot 10^{-4} \cdot 1.25 \cdot 0.75 \cdot 10^{3}]/[w/c-0.14] +1\}$

$\delta_{eff} = 2 \cdot 10^{-10} \cdot \{(w/c-0.29)/(w/c+0.32)\}/\{[6.3 \cdot 10^{-4} \cdot 1.25 \cdot 0.75 \cdot 10^{3}]/[w/c-0.29] +1\}$

The results are shown in the table and figure.

w/c	All pores eq (A15)		Capillary pores eq (A17)	
	δ_{eff} m^2/s	δ_{eff} in relation to w/c 0.40	δ_{eff} m^2/s	δ_{eff} in relation to w/c 0.40
0.4	$4.9 \cdot 10^{-12}$	1	$4.9 \cdot 10^{-12}$	1
0.5	$7.4 \cdot 10^{-12}$	1.5	$13.4 \cdot 10^{-12}$	2.7
0.6	$9.8 \cdot 10^{-12}$	2.0	$23.2 \cdot 10^{-12}$	4.7
0.7	$11.9 \cdot 10^{-12}$	2.4	$33.0 \cdot 10^{-12}$	6.7
0.8	$13.9 \cdot 10^{-12}$	2.8	$42.2 \cdot 10^{-12}$	8.6
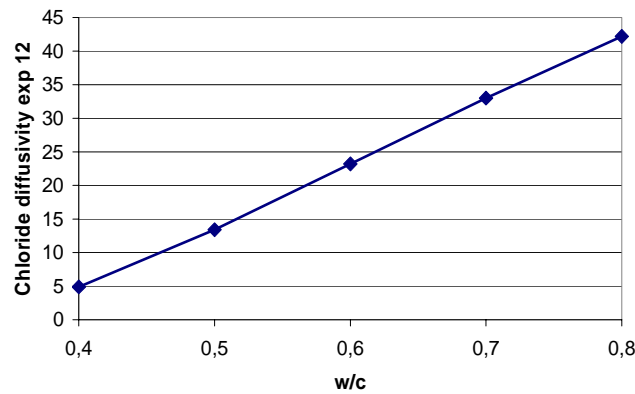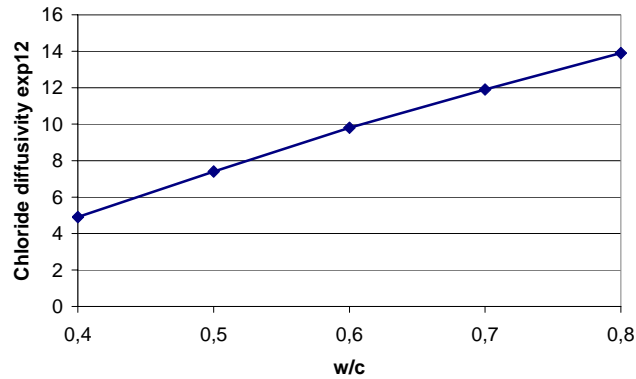
Upper figure: All pores take part in chloride transport
Lower figure: Only capillary pores take part in chloride transport

Example A4: Effect of the degree of hydration on the diffusion coefficient

Assumptions
- w/c-ratio 0.40
- Outer chloride concentration c=0.4 mole/litre. Gives $c_{b,gel}/c=9 \cdot 10^{-3}/14.2=$
  $=6.3 \cdot 10^{-4}$ (Figure 4, Table A1)
- K=$4.5 \cdot 10^{-11}$ m^2/s
- All pores are assumed to take part in chloride transport.

Equation (A15) is applied:
$\delta_{eff} = 4.5 \cdot 10^{-11} \cdot \{(w/c-0.19\alpha)/(w/c+0.32)\}/\{[6.3 \cdot 10^{-4} \cdot 1.25\alpha \cdot 10^{3}]/[w/c-0.19\alpha] +1\}$

The results are shown in the table and figure.

Degree of hydration	δ_{eff} m^2/s
0.25	$14 \cdot 10^{-12}$
0.50	$8.2 \cdot 10^{-12}$
0.75	$4.9 \cdot 10^{-12}$
1.00	$2.7 \cdot 10^{-12}$
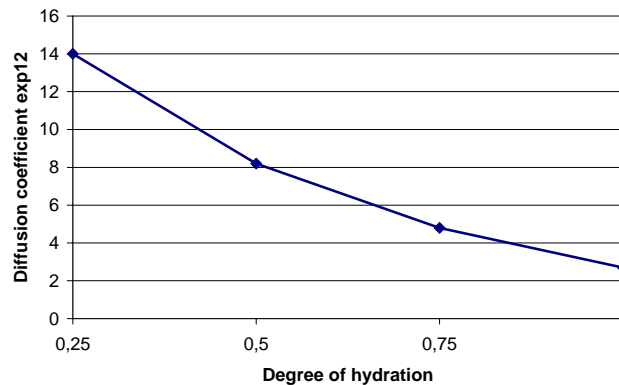
According to experimental data in Frederiksen et al. (1997) -see Figure A11- the diffusion coefficient is increased by a factor 3 at an increase of the w/c-ratio from 0.4 to 0.8 (from $8 \cdot 10^{-12}$ to $24 \cdot 10^{-12}$ m^2/s). This is almost identical with the theoretical results in the example when *all pores* are supposed to be active in chloride transport.
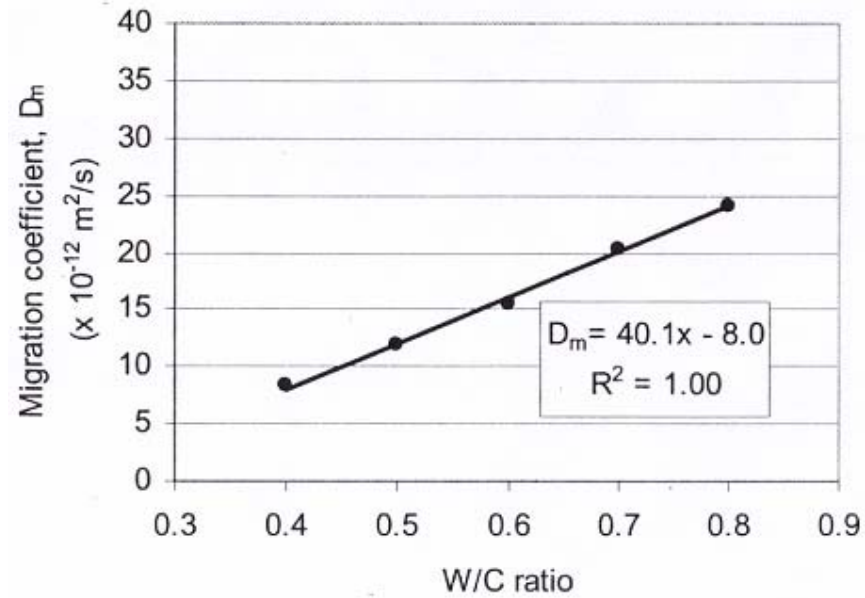

Figure A11: Experimental determination of the relation between the chloride migration coefficient and the water-cement ratio. Frederiksen et al. (1997)

A2.3 Imaginable effects of limestone filler

As described in paragraph 4, limestone filler might affect the steady state diffusion coefficient δ_0. Such an effect can be determined by the test described in paragraph 5.2. Any change in δ_0 caused by limestone filler will be revealed by a change in the coefficient K in equations (A15) and (A17).

As said in paragraph A1.3 limestone filler might also affect the porosity, but as a first approximation this is neglected. Thus, equations (A15) and (A17) can be assumed to be valid also for concrete with limestone filler, provided the effect of filler on the parameters δ_0 and $c_{b,gel}$ are considered.

ANNEX 3

EVALUATION OF A DIFFUSION CELL TEST

Consider the diffusion cell below.
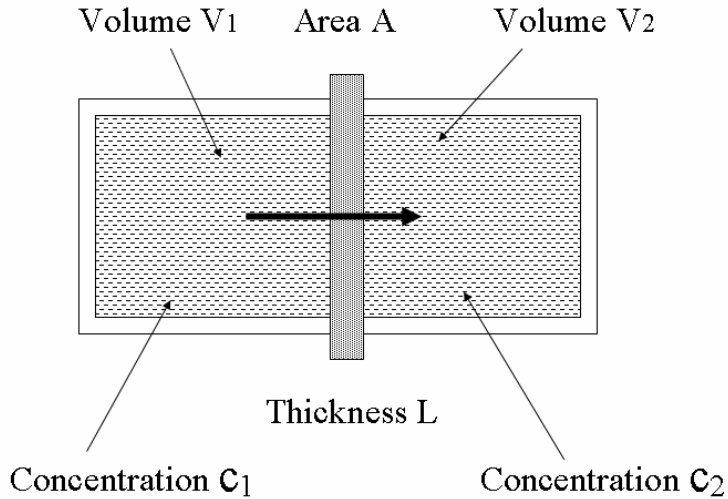
After an "incubation time", during which chloride is bound in the sample, the rate of decrease in chloride concentration in chamber 1 equals the rate of chloride increase in chamber 2.Then steady state conditions are prevailing. The figure below shows the steady state flow. Flow is counted from time zero which corresponds to the first measurement of chloride concentration in the two chambers. At time 0 the concentration in chamber 1 is $c_1 = c_{1,0}$. The concentration in chamber 2 is $c_2 = c_{2,0}$. After the additional time Δt a chloride an additional steady state flow ΔQ has taken place. The new chloride concentrations in the two chambers are $c_1 = c_{1,1}$ and $c_2 = c_{2,1}$.
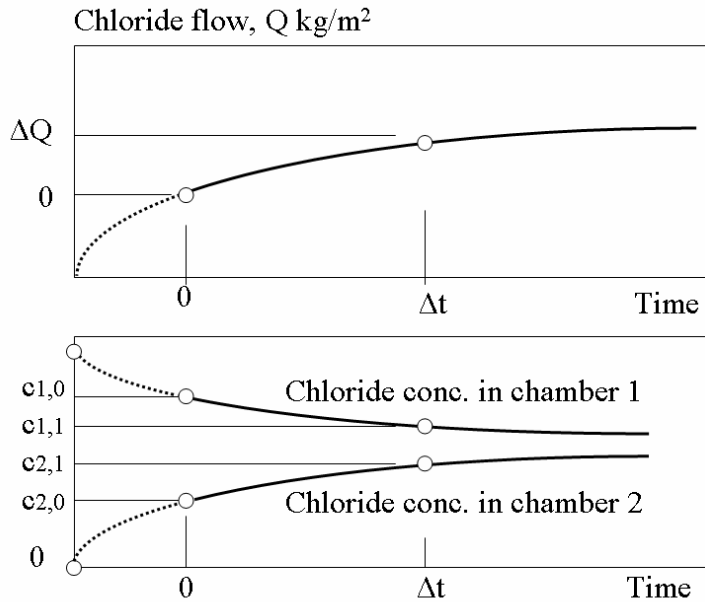
Chloride transport at steady state is:

$$dQ/dt = (\delta_0/L)(c_1 - c_2) \tag{A18}$$

The concentrations in the two chambers are:

$$c_1 = c_{1,0} - Q \cdot A/V_1 \tag{A19}$$

$$c_2 = c_{2,0} + Q \cdot A/V_2 \tag{A20}$$

Where $c_{1,0}$ and $c_{2,0}$ are the "initial" concentrations in chambers 1 and 2. Q is the total flow from that point.

Combining the three equations give:

$$dQ/dt = (\delta_0/L)[(c_{1,0} - Q \cdot A/V_1) - (c_{2,0} + Q \cdot A/V_2)] \tag{A21}$$

Separation of the equation gives:

$$\int_0^{\Delta Q} dQ/[c_{1,0} - c_{2,0} - (A/V_1 + A/V_2)Q] = \int_0^{\Delta t} (\delta_0/L)dt \tag{A22}$$

Where ΔQ is the chloride flow between the first observations of chloride at time 0 ($c_{1,0}$ and $c_{2,0}$) and the concentrations at time Δt ($c_{1,1}$ and $c_{2,1}$).

Integration gives:

$$-V_1 \cdot V_2/[(V_1 + V_2)A] \cdot \ln[c_{1,0} - c_{2,0} - (A/V_1 + A/V_2)\Delta Q] + V_1 \cdot V_2/[(V_1 + V_2)A] \cdot$$
$$\cdot \ln[c_{1,0} - c_{2,0}] = (\delta_0/L) \cdot \Delta t \tag{A23}$$

or

$$\delta_0 = (L/\Delta t) \cdot V_1 \cdot V_2/[(V_1 + V_2)A] \cdot \ln\{(c_{1,0} - c_{2,0})/[c_{1,0} - c_{2,0} - (A/V_1)\Delta Q - (A/V_2)\Delta Q]\} \tag{A24}$$

According to equations (A19) and (A20) the following relations are valid:

$$(A/V_1)\Delta Q = c_{1,0} - c_{1,1} \tag{A25}$$
$$(A/V_2)\Delta Q = c_{2,1} - c_{2,0} \tag{A26}$$

Inserting these equations in equation (A24) gives:

$$\boldsymbol{\delta_0 = (L/\Delta t) \cdot V_1 \cdot V_2/[(V_1 + V_2)A] \cdot \ln\{(c_{1,0} - c_{2,0})/(c_{1,1} - c_{2,1})\}} \tag{A27}$$

Thus, the diffusion coefficient can be determined by measurements of the chloride concentrations in the two chambers at two different occasions.

At steady state conditions the flow out from chamber 1 equals the flow into chamber 2. Therefore, there is a relation between the concentrations in the two chambers. Combining equations (A19) and (A20) gives the following relations:

$$c_{2,1} - c_{2,0} = (c_{1,0} - c_{1,1})(V_1/V_2) \qquad (A28)$$

$$c_{1,0} - c_{1,1} = (c_{2,1} - c_{2,0})(V_2/V_1) \qquad (A29)$$

These equations can be used for control that steady state has been reached.

Equation (A27) can be simplified when the two chambers are of equal volume, V:

$$\boldsymbol{\delta_0 = (L/\Delta t) \cdot V/(2A) \cdot \ln\{(c_{1,0} - c_{2,0})/(c_{1,1} - c_{2,1})\}} \qquad (A30)$$
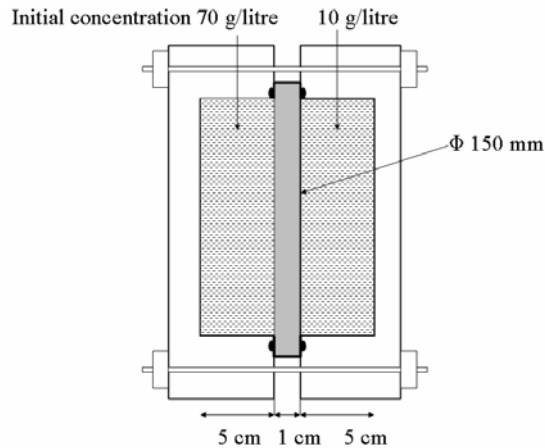

Example A5

A cylinder-shaped diffusion cell has the following dimensions, see the figure.
- Diameter of diffusion area: 15 cm
- Diffusion area, A: $1.77 \cdot 10^{-2}$ m^2
- Chamber depth: 5 cm
- Chamber volumes, V: $1.77 \cdot 10^{-2} \cdot 5 \cdot 10^{-3} = 8.9 \cdot 10^{-5}$ m^3
- The specimen thickness: L=1 cm=10^{-2} m

The initial concentrations are:
- $c_{1,0}$=70 g/litre
- $c_{2,0}$=10 g/litre

Initial concentration 70 g/litre   10 g/litre

Φ 150 mm

5 cm   1 cm   5 cm

30 days ($2.59 \cdot 10^6$ s) after the first measurement the following concentrations are obtained:
- $c_{1,1}$=50 g/litre
- $c_{2,1}$=30 g/litre (according to equation (A29) steady state has been reached)

The diffusion coefficient becomes:

$\delta_0 = (10^{-2}/2.59 \cdot 10^6) \cdot 8.9 \cdot 10^{-5}/(2 \cdot 1.77 \cdot 10^{-2}) \cdot \ln\{(70-10)/(50-30)\} = \boldsymbol{1.1 \cdot 10^{-11}}$ **m²/s**

Concentrations $c_{1,1}$ and $c_{2,1}$ to be expected after an arbitrary duration Δt can be calculated by the following equation, provided the diffusivity is known:

$$c_{1,0}\text{-}c_{2,0}/(c_{1,1}\text{-}c_{2,1})=\exp\{\delta_0\cdot 2A\cdot\Delta t/(L\cdot V) \qquad\qquad \textbf{(A31)}$$

According to equations (A28) or (A29):

$\quad c_{1,1}=c_{1,0} - c_{2,1} + c_{2,0}$
which gives:
$\quad c_{1,1}\text{-}c_{2,1} =\Delta c=(c_{1,0}\text{-} c_{2,1} +c_{2,0}) \text{-}c_{2,1}$
from which:

$$c_{2,1}=(c_{1,0}+c_{2,0}\text{-}\Delta c)/2 \qquad\qquad\qquad\qquad\qquad\qquad (A32)$$

and

$$c_{1,1}=\Delta c+c_{2,1} \qquad\qquad\qquad\qquad\qquad\qquad\qquad (A33)$$

Example A6
The same as Example A5. The concentration curves are calculated

Example: Calculation for $\Delta t=60$ days ($5.18\cdot10^6$ s) is performed.
Equation (A31) gives:
$(70\text{-}10)/(c_{1,1}\text{-}c_{2,1})=\exp\{1.1\cdot10^{-11}\cdot 2\cdot1.77\cdot10^{-2}\cdot5.18\cdot10^6)/(10^{-2}\cdot8.9\cdot10^{-5})\}=9.64$
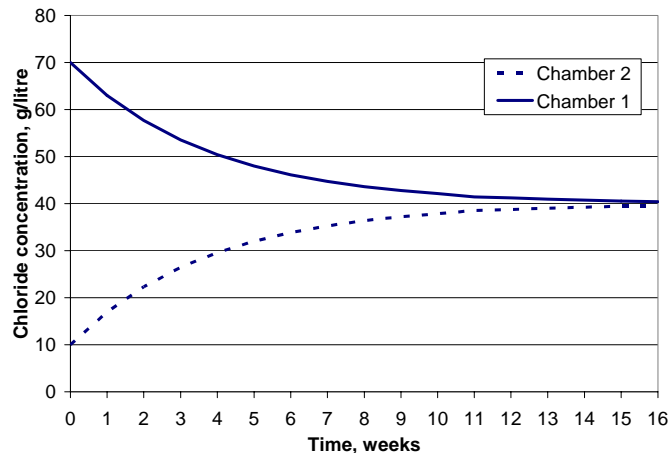$c_{1,1}\text{-}c_{2,1}=(70\text{-}10)/9.64=6.2$ g/litre

Equations (A32) and (A33) give:
$c_{2,1}=(70+10\text{-}6.2)/2=36.9$ g/litre
$c_{1,1}=6.2+36.9 \qquad =43.1$ g/litre

The expected chloride concentration curves for the two chambers are shown in the figure below.

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ANNEX 4

DETERMINATION OF THE "ACTIVE" POROSITY FOR DISSOLVING CHLORIDE

One possibility to determine the fraction of pore water participating in the dissolution of chloride is to use the hypothesis (strengthened by Figure 4) that a unit weight of the "cement gel" (hydration product) always binds the same amount of chloride at a given free chloride ocentration. This quantity is denoted $c_{b,gel}$ (g/g).

This means that the total amount of bound chloride Q_{bound} (g) can be determined by (for OPC):

$$Q_{bound} = c_{b,gel} \cdot Q_{gel}' = c_{b,gel} \cdot 1.25 \cdot \alpha \cdot C' \cdot V \qquad (A34)$$

Where Q_{gel}' is the amount of cement gel in the specimen (g). It is given by equation (13). α is the degree of hydration, C' is the cement content (g per cm^3) and V the specimen volume (cm^3).

The pore water quantity dissolving chloride w_w (cm^3=g) is:

$$w_w = C' \cdot (W/C - \gamma \cdot \alpha) \cdot V \qquad (A35)$$

Where $0.19 < \gamma < 0.39$. $\gamma = 0.19$ means that all pore water dissolves chloride while $\gamma = 0.39$ means that only capillary water is available as solvent. The equation is valid for OPC.

The free chloride content Q_{free} (g) becomes:

$$Q_{free} = c''' \cdot w_w = c''' \cdot C' \cdot (W/C - \gamma \cdot \alpha) \cdot V \qquad (A36)$$

where c''' is the chloride concentration in the bath (the same as in the pore water) (g/cm^3)

The total chloride content is determined experimentally. It becomes:

$$Q_{tot} = Q_{bound} + Q_{free} = c_{b,gel} \cdot 1.25 \cdot \alpha \cdot C' \cdot V + c''' \cdot C' \cdot (W/C - \gamma \cdot \alpha) \cdot V \qquad (A37)$$

From this equation the coefficient $c_{b,gel}$ can be solved

$$\mathbf{c_{b,gel} = [Q_{tot} - c''' \cdot C' \cdot (W/C - \gamma \cdot \alpha) \cdot V / [1.25 \cdot \alpha \cdot C' \cdot V]} \qquad (A38)$$

All parameters on the right hand side except γ are known. By testing many specimens with different w/c-ratio in a chloride solution of constant strength, $c''' =$ constant, a value of γ that gives almost the same value of $c_{b,gel}$ valid for the actual strength might be found.

For each experiment the relation between γ and $c_{b,gel}$ is calculated. Theoretically, all these relations will intersect at one single value of γ. This value describes the fraction of pore water that is available for dissolving chloride. The principles are shown in Figure A12.

Note: Equation (13) and consequently equation (A34), and equation (A35) are supposed to be valid for OPC-concrete. Other cements can produce other types and other amount of hydration products and other porosity. Since the reaction products of limestone filler are assumed to be of marginal volume it is assumed that the equations can also be used for concrete with limestone filler. Therefore, α expresses the degree of hydration of the OPC in the concrete. w/c in the equations is counted only on the OPC in the concrete. C is the OPC-content.
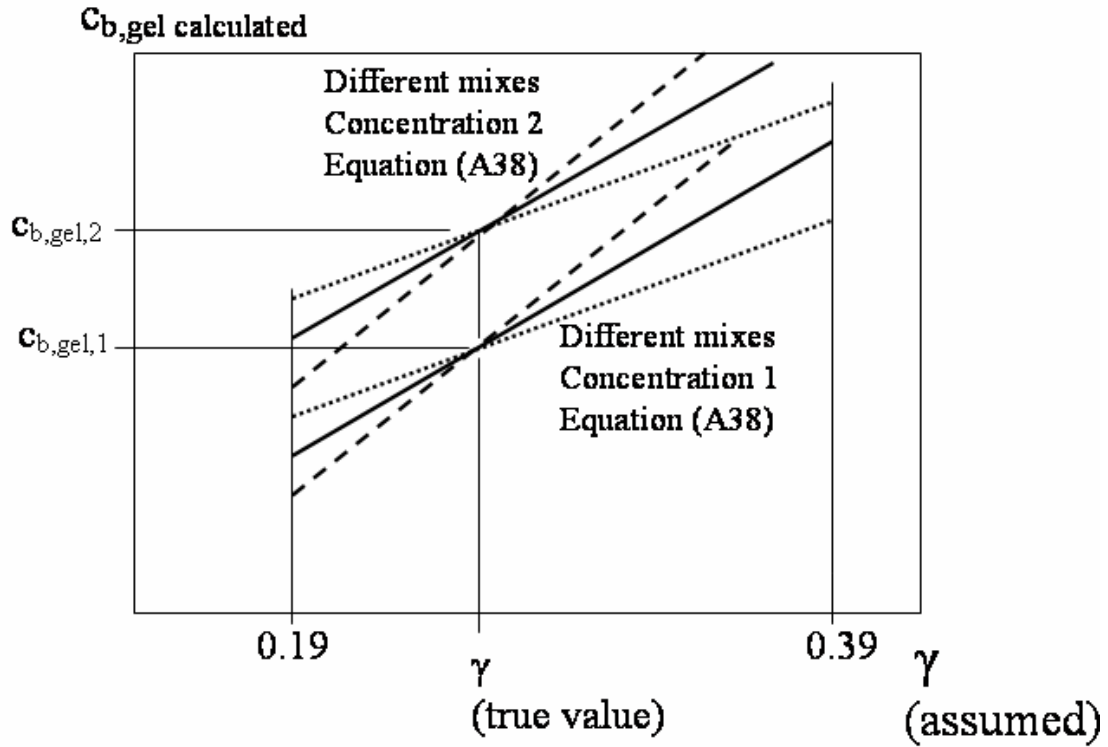

Figure A12: Determination of the coefficient γ in equation (A38).