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Fagerlund, Göran

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LUND UNIVERSITY

PO Box 117
221 00 Lund
+46 46-222 00 00

LUND INSTITUTE OF TECHNOLOGY
LUND UNIVERSITY

Division of Building Materials

The threshold chloride level for initiation of reinforcement corrosion in concrete

Some theoretical considerations

Göran Fagerlund

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Lund Institute of Technology
Division of Building Materials
Box 118
SE-221 00 Lund, Sweden

Telephone: 46-46-2227415
Telefax: 46-46-2224427
www.byggnadsmaterial.lth.se

SUMMARY

The report is based on the assumption that reinforcement corrosion is initiated when the free chloride concentration in pore water surrounding the bar has reached a certain critical level, which is proportional to the OH^- -ion concentration in the pore water; Eq. (1). According to Hausmann (1967) the proportionality coefficient K is supposed to be 0.6. Other values are imaginable, depending on such factors as w/c-ratio, cement composition and thickness of cover.

Formulas are presented in the report for calculation of:

1. The *threshold chloride concentration in pore water* (mole/litre or g/litre). It depends on *two coefficients*; K and k.
2. The *threshold total chloride content (bound+free) expressed as weight-% of cement.* It depends on *four coefficients*. Two of these depend on the alkalinity of the concrete; K and k. Two coefficients depend on the chloride binding capacity; a and b; see Eq. (16).

The equations are applicable to any value of the threshold chloride concentration versus OH^--ion concentration (coefficient K), to any value of the water soluble alkali content in the cement (coefficient k), and to any water-cement ratio and age of the concrete.

Formulas are derived for many scenarios:

- Different alkalinity of cement (coefficient k in Eq. (3)).
  Paragraphs 5. and 7.
- Different critical chloride concentration for start of corrosion (coefficient K in Eq. (1)).
  Paragraph 8.
- Different chloride binding capacity of cement gel.
  Paragraph 9.
- Different degree of hydration (concrete age).
  Paragraph 10.
- Different amount of limestone filler in cement.
  Paragraph 11.
- Different types and amount of mineral admixtures in cement.
  Paragraph 12.
- Total or partial leaching of alkali from the concrete.
  Paragraph. 13.
  A theory for calculation of the rate of leaching is presented in APPENDIX 2.
- Different moisture content in the concrete (different RH).
  Paragraph 14.
- Corrosion of steel in carbonated concrete.
  Paragraph 15.

Furthermore, a *qualitative discussion* of the effect of the following factors is performed:

- Effect of the cover thickness.
  Paragraph 16.
- Effect of defect bond.
  Paragraph 17.

The threshold chloride value depends on how Cl$^-$-ions and OH$^-$-ions are distributed within the pore system. Three alternatives are imaginable, Figure 1. Alternative 3 seems most logical. Therefore, most examples in the report are based on Alternative 3. However, formulas are given for all three alternatives. Examples of calculated threshold values for two cement types based on the three alternatives are given in Tables 6 and 7. An experimental method to determine which alternative is valid is presented in APPENDIX 1.

Examples of calculated threshold chloride content as weight-% of cement are given in the tables below. The water-cement ratio is 0.40 and the degree of hydration 65%. The ion-distribution is assumed to be described by Alternative 3.

High alkali cement $(Na_2O)_{equiv.}$*=1.29 %. High critical threshold conc.; K=0.60 (Eq. (1).)*

Threshold value, weight-% of cement				
Effect of binding capacity, Eq. (16)		Effect of 30% limestone. High binding cap.	Effect of 10% silica fume High binding cap.	Effect of drying to RH=80% High binding cap.
High, a=13.5	Low, a=6.75			
1.52	**1.00**	**1.32**	**0.66**	**1.45**

High and low alkali cement. Effect of critical [Cl$^-$]/[OH$^-$]-ratio. High and low critical threshold conc.; K=0.60 and 0.40 (Eq. (1).) High binding capacity.

Threshold value, weight-% of cement			
K=0.60		K=0.40	
High alkali cement 1.29	Low alkali cement 0.5%	High alkali cement 1.29%	Low alkali cement 0.5%
1.52	**0.89**	**1.20**	**0.72**

The calculations indicate the following interesting observations regarding the threshold content of *total chloride in weight-% of cement*:

- The threshold chloride content is of the order 1.0 to 1.5 weight-% of cement for mature concrete made with high alkali Portland cement $(Na_2O)_{equiv}\approx 1.3\%$.
- The threshold chloride content is of the order 0.7 to 0.9 weight-% of cement for mature concrete made with low alkali Portland cement $(Na_2O)_{equiv}\approx 0.5\%$.
- The effect of water-cement ratio is very small for mature concrete.
- The effect of 50% reduction in binding capacity, Eq. (16), or 50% reduction in threshold concentration, K in Eq. (1), gives only about 40% reduction in the chloride threshold value.
- The negative effect of limestone and silica fume in cement is big
- The effect of drying is marginal.

The effect of water-cement ratio, cement alkalinity (k) and threshold concentration (K) on the threshold concentration of *free chloride in g/litre* (or mole/litre) is big. Examples are shown in the table below. The ion-distribution is assumed to be described by Alternative 3.

w/c	**Threshold concentration in pore water (g/litre)**			
	High alkali cement $(Na_2O)_{equiv.}$=1.29 %.		Low alkali cement $(Na_2O)_{equiv.}$=0.5 %.	
	K=0.6	K=0.4	K=0.6	K=0.4
0.6	**20**	**13**	**7**	**5**
0.5	**24**	**16**	**9**	**6**
0.4	**32**	**21**	**12**	**8**
0.3	**43**	**29**	**17**	**11**

CONTENTS

LIST OF SYMBOLS
(Except formulas in APPENDIX 1)

a	Coefficient in the binding isotherm Eq. (16)
b	Coefficient in the binding isotherm Eq. (16)
c_{free}	Concentration of free chloride in pore water (mole/litre), Eq. (16)
c_{bound}	Amount of bound chloride (mg/g cement gel), Eq. (16)
$c_{bound,AFm}$	Bound chloride in the Arm-phase in cement (mole Cl^-/mole AFm)
$c_{bound,CSH}$	Bound chloride in CSH-gel (mole Cl^-/g CSH-gel)
g	Weight fraction of inert filler in cement (-)
h	Amount of hydration product, Eq. (38) (kg/kg hydrated cement)
k	Amount of alkali (Na_2O and K_2O) in cement expressed as OH^--ions (mole/kg cement)
w_{cap}	The capillary pore volume, Eq. (4), (litres or litres/m^3 of concrete)
w_{tot}	The total pore volume in concrete, Eq. (5), (litres or litres/m^3 of concrete)
w_o/c	Water-cement ratio (-)
$(w_0/c)_{eff}$	Effective water-cement ratio defined by Eq. (31) (-)
w_e/c	Amount of pore water (kg/kg cement)
C	Cement content (kg)
K	Relation between threshold chloride concentration and OH^--concentration, Eq. (1)
Na_2O_{eq}	Amount of $Na_2O + 0.66 \cdot K_2O$ (weight-% of cement)
PC	Amount of Portland component in cement (kg)
Q_{gel}	Weight of cement gel (kg)
$V_{P,Cl}$	Volume of pore water able to dissolve chloride, Eq. (46) (litres/m^3 of concrete)
$[Cl^-{}_{free}]_{thr}$	Concentration of free chloride ions in pore water (mole/litre)
$[OH^-]$	Concentration of OH^--ions in pore water (mole/litre)
$(Cl^-{}_{free})_{thr}$	Amount of free chloride ions at threshold concentration (g/litre pore water)
$(Q_{Cl^- free})_{thr}$	Amount of free chloride ions at threshold concentration (kg)
$(Q_{Cl^- bound})_C$	Amount of bound chloride ions (weight-% of cement)
$(Q_{Cl^- total})_C$	Total amount of bound+free chloride ions (weight-% of cement)
$(Q_{Cl^- free})_C$	Amount of free chloride ions (weight-% of cement)
$(Q_{Cl^- free})_{C,thr}$	Amount of free chloride ions at threshold concentration (weight-% of cement)
$(Q_{Cl^- bound})_{C,thr}$	Amount of bound chloride at threshold concentration (weight-% of cement)
$(Q_{Cl^- total})_{C,thr}$	Total amount of chloride at threshold concentration (weight-% of cement)
α	Degree of hydration (-)
β	Degree of reaction of cement, Eq. (38) (-)

1. BASIC ASSUMPTIONS

The analysis below is based on the following two assumptions:

1. Start of corrosion is determined by the *free* chloride concentration in pore water surrounding the reinforcement bar. The total chloride content is supposed to be of no importance[1].

2. The threshold concentration of free chloride content is supposed to be directly proportional to the OH-ion concentration of the pore solution:

$$\boxed{\left[Cl^-{}_{free}\right]_{thr} = K \cdot \left[OH^-\right] \quad \text{mole/litre.} \qquad (1)}$$

where K is a coefficient which might depend on many parameters, such as the chemical composition of the pore solution, the oxygen concentration in pore water surrounding the reinforcement bar, and the type of steel.

According to Hausmann (1967) the constant K is about 0.6 for ordinary steel immersed in bulk chloride solution, i.e.:

$$\left[Cl^-{}_{free}\right]_{thr} \approx 0.6 \cdot \left[OH^-\right] \quad \text{mole/litre} \qquad (2)$$

2. DISSOLUTION OF ALKALI AND CHLORIDE IN PORE WATER – THREE ALTERNATIVES

The pore system of cement paste is divided in two parts:

1. The extremely narrow gel pores containing pores with average width about 15 Å
2. The coarser capillary pores with pore size varying from about 50 Å to 1000 Å.

There are two extreme possibilities for water soluble alkali oxides in cement (Na_2O and K_2O), to be dissolved. As one extreme, all alkali is evenly dissolved in water present in the entire pore system (Alt 2 and 3 in Figure 1). As the other extreme it is only dissolved in the capillary pore water (alt 1 in Figure 1).

Similarly, chloride ions might be dissolved, either in all pore water (Alt 2 in Figure 1), or only in the capillary water (Alt 1 and 3 in Figure 1).

The threshold concentration will depend on how the dissolution of alkali and chloride takes place as will be shown below.

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[1] The total chloride content, which is the sum of free and bound chloride, is however of big importance for the diffusion rate of chloride in the pore system; the higher the fraction of bound chloride, the lower is the effective diffusion coefficient. Therefore, bound chloride affects the *service life* of the concrete with regard to chloride induced corrosion despite the fact that it does not affect the threshold concentration. The present report only deals with the threshold concentration.

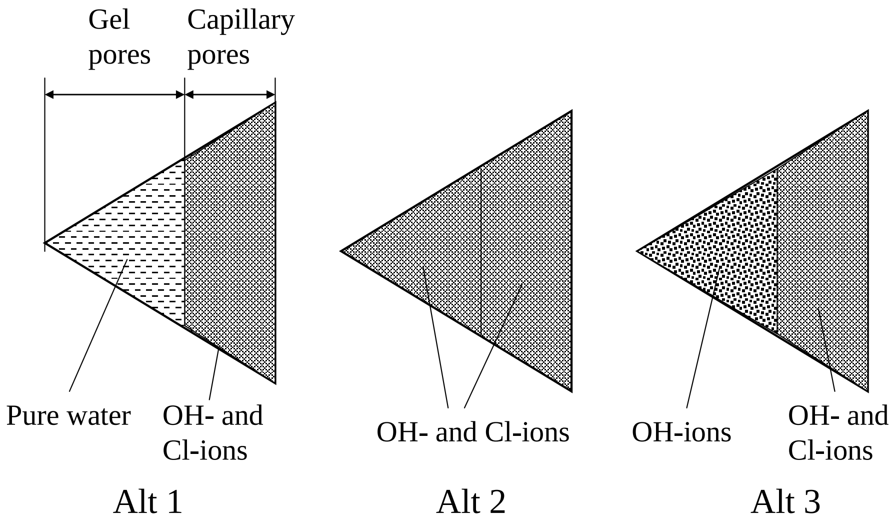

Figure 1. Different alternatives for dissolution of alkali and chloride.

Alternative 3 is most plausible for the following reasons:

1. Alkali is dissolved rapidly when cement comes in contact with water during concrete mixing. Thus it is reasonable to assume that all pore water is alkaline already from early age.
2. Chloride ions enter the concrete when the solid structure has already developed. It seems reasonable to assume that the ions cannot easily penetrate the very narrow entrances to gel pores. For example it has been shown experimentally that nitrogen vapour cannot enter gel pores, while the smaller water molecules can, and that organic liquids cannot enter gel pores, Powers (1962).

An experimental method to determine which pores are available for dissolving chloride is suggested in the APPENDIX.

3. THE THRESHOLD CONTENT OF *FREE* CHLORIDE - THEORY

Concrete based on ordinary Portland cement is treated in this paragraph. Therefore, known formulae for capillary porosity and total porosity of Portland cement paste can be used. Water-cement ratio is defined in the normal way as w_o/c where w_o is the amount of mixing water (kg) and c is the amount of cement (kg). The effect of other types of binders is discussed in paragraphs x and y.

The amount of water soluble alkali *in cement* expressed as OH^--ions is

k mole /kg cement

The amount of water soluble OH^--ions *in concrete* is:

$$OH^- = k \cdot C \quad \text{mole} \qquad (3)$$

where C is the cement content.

The volume of pore water able to dissolve alkali depends on the degree of saturation of the concrete. Only complete saturation is considered in the present paragraph because this is "the most dangerous case" (lowest OH^--concentration). Non-saturated concrete is treated in paragraph 14.

The amount of water able to dissolve alkali can correspond either to the capillary pore volume (Alt 1) or to the entire pore volume (Alt 2 and Alt 3) [2].

Alt 1: Only water in capillary pores dissolves alkali. The volume of this water is:

$$w_{cap} = w_0 - 0.39 \cdot \alpha \cdot C = C \cdot \left(\frac{w_0}{C} - 0.39 \cdot \alpha \right) \text{ litres} \tag{4}$$

where
w_0 is the amount of mixing water (litres/m^3 concrete)
α is the degree of hydration of the cement (-)

Alt 2 and Alt 3: All pore water dissolves alkali. The volume of this water is:

$$w_{tot} = w_0 - 0.19 \cdot \alpha \cdot C = C \cdot \left(\frac{w_0}{C} - 0.19 \cdot \alpha \right) \text{ litres} \tag{5}$$

The concentration of OH^- in pore water becomes:

Alt 1:

$$\left[OH^-\right] = \frac{k \cdot C}{w_0 - 0.39 \cdot \alpha \cdot C} = \frac{k}{w_0 / c - 0.39 \cdot \alpha} \text{ mole/litre} \tag{6}$$

where w_o/c is the water-cement ratio.

Alt 2 and Alt 3:

$$\left[OH^-\right] = \frac{k \cdot C}{w_0 - 0.19 \cdot \alpha \cdot C} = \frac{k}{w_0 / c - 0.19 \cdot \alpha} \text{ mole/litre} \tag{7}$$

The threshold concentration of free chloride ions becomes:

Alt 1:

$$\boxed{\left[Cl^-\right]_{thr} = \frac{K \cdot k}{w_0 / c - 0.39 \cdot \alpha} \text{ mole/litre}} \tag{8}$$

---

[2]) It is assumed that air pores do not contain water. In reailty, during very moist conditions, a fraction of the air-pore system might be water-filled for longer or shorter periods; see the analysis in Fagerlund (2004). This means that the alkalinity of pore water might be lower and therefore also the threshold concentration be lower than the values calculated below. The effect is however limited, which is shown by the following example:
For a concrete with w/c-ratio 0.40, cement content 420 kg/m^3, and air content 5%, 30% of which is water-filled, the total porosity (exclusive of air-pores) is about 115 litres/m^3 (porosity 11.5%). The water-filled air-pore volume is 15 liter/m^3. Thus, the water volume is increased by about 13%. The decrease in OH^--concentration and threshold concentration is also about 13%.

Alt 2 and Alt 3:

$$\left[Cl^-\right]_{thr} = \frac{K \cdot k}{w_0 / c - 0.19 \cdot \alpha} \quad \text{mole/litre} \tag{9}$$

The threshold concentration expressed as *weight* of chloride ions is given by Eq. (8) and (9) multiplied by the mole weight of chlorine 35.5 g/mole:

Alt 1:

$$\left(Cl^-{}_{free}\right)_{thr} = \frac{K \cdot k \cdot 35.5}{w_0 / c - 0.39 \cdot \alpha} \quad \text{g/litre} \tag{10}$$

Alt 2 and Alt 3:

$$\left(Cl^-{}_{free}\right)_{thr} = \frac{K \cdot k \cdot 35.5}{w_0 / c - 0.19 \cdot \alpha} \quad \text{g/litre} \tag{11}$$

Assuming the Hausmann criterion to be valid (i.e. K=0.6), the threshold concentration calculated by these equations is given in Table 1 and plotted in Figure 2.

Table 1: The threshold concentration of free chloride ions in saturated portland cement concrete. The degree of hydration selected is normal for concrete a couple of months old. The values are based on the Hausmann criterion (i.e. K=0.6).

w_o/c	α	Threshold amount of chloride ions [1)] $\left(Cl^-{}_{free}\right)_{thr} / k$	
		Alt 1 Only capillary water dissolves alkali	Alt 2 and Alt 3 All water dissolves alkali
0.60	0.75	**69**	**47**
0.50	0.70	**94**	**58**
0.40	0.65	**145**	**77**
0.30	0.50	**203**	**104**

1) The unit is: $\dfrac{g\ Cl^- / litre\ \ pore\ water}{mole\ OH^- / kg\ cement}$

The theoretical analysis shows that the threshold concentration of free chloride increases with decreasing w/c-ratio, which is a consequence of the fact that a decreased w/c-ratio means a decreased porosity and therefore an increased OH^--concentration.

For Alt 3, which is the most plausible of the three alternatives, a decrease of the w/c-ratio from 0.6 to 0.4 causes an increase in the threshold concentration by 40%, which is of course very favourable with regard to decreasing the risk of chloride induced corrosion..

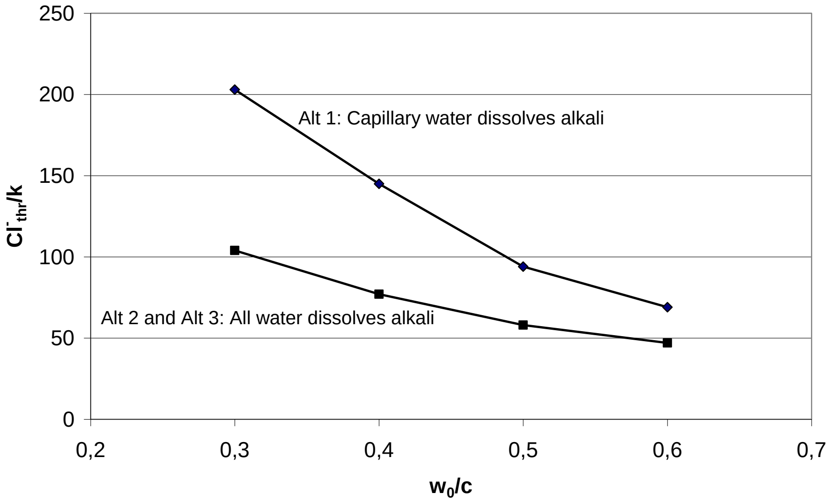

Figure 2: Calculated threshold level of free chloride in saturated Portland cement based on the Hausmann criterion. Data from Table 1.

4. COMPARISON OF THEORY WITH EXPERIMENT

According to the theory above the threshold value increases with decreased water/cement ratio. This has also been observed experimentally by Pettersson (1994); see Figure 3. The determination was made for saturated concrete.

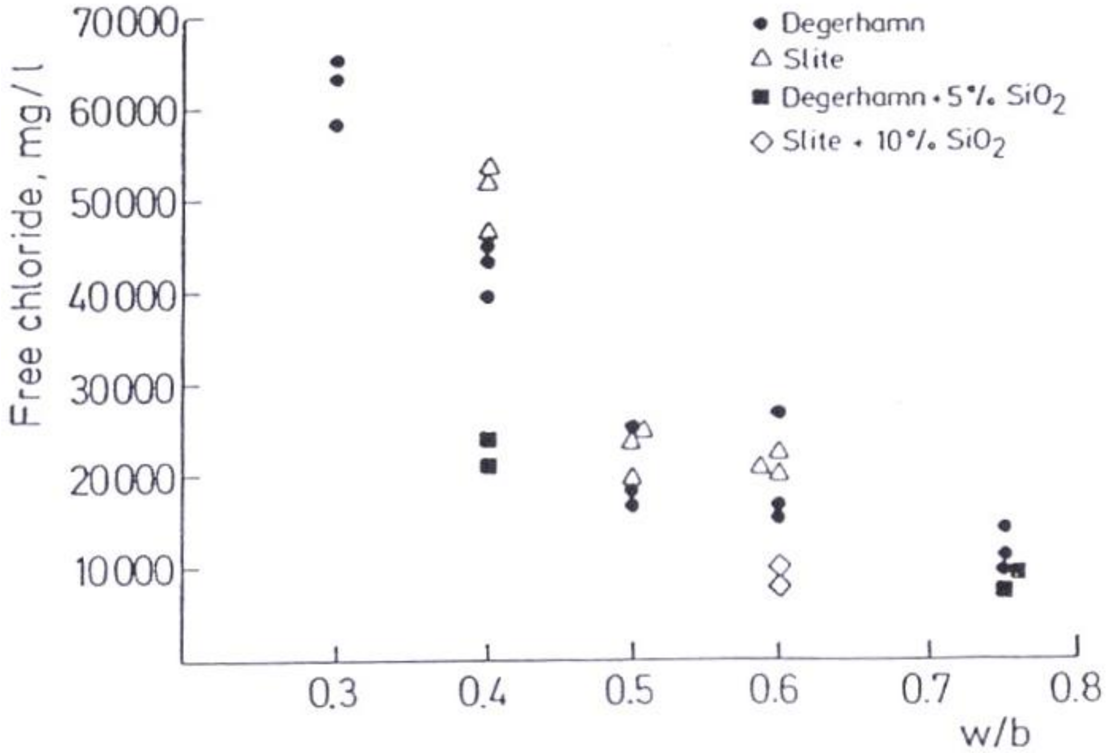

Figure 3: Measured threshold concentration of free chloride, Pettersson (1994). Degerhamn: Low alkali cement (0.5%). Slite: High alkali cement (1.29%). SiO_2: Silica fume.

In Table 2 theoretically calculated threshold values from Table 1 are compared with experimentally determined threshold values from Figure 2. Comparisons are made with threshold concentration for water/cement ratio 0.40.

Table 2: Relative values of the free chloride concentration in water saturated concrete. Theoretical values from Table 1 and measured values from Figure 2. Only data for ordinary Portland cement (OPC) are used in the comparison. Concrete with low alkali/sulphate resistant cement and concrete with silica fume are omitted since these binders have different amount of alkali.

w_o/c	$\left(Cl^-{}_{free}\right)_{thr}$ theoretical from Table 1 (% of value for $w_0/c=0.40$)		$\left(Cl^-{}_{free}\right)_{thr}$ experimental from Figure 3 (% of value for $w_0/c=0.40$)
	Alt 1	Alt 2 and Alt 3	
0.60	**48**	**61**	38-48 (average 42)
0.50	**65**	**75**	38-52 (average 45)
0.40	**100**	**100**	100
0.30	**140**	**135**	Information lacking

Both the theoretical analysis and the experimental finding indicate that the threshold concentration is not a constant but that it increases with decreased water/cement ratio. When total chloride is used as criterion for onset of corrosion, which normally is the case at calculation of service life, one single value is normally used for all water/cement ratios.

5. QUANTITATIVE THRESHOLD VALUES OF *FREE* CHLORIDE

As shown above, the OH-ion concentration of pore water and therefore the threshold concentration of free chloride are determined by two main factors:

1. The amount of water-soluble Na_2O and K_2O in the cement.
2. The amount of pore water able to dissolve alkali. There are two possibilities, see Figure 1. Alt 1 where only capillary water is “active”, and Alt 2 and Alt 3 where all water acts as solvent

When all Na_2O and K_2O has been completely leached out the OH^--concentration is determined by the saturation pH of $Ca(OH)_2$, which is about 12.3. This corresponds to the OH^--concentration 0.02 mole/litre.

5.1 HIGH-ALKALI CEMENT

Swedish Portland cement used for the concrete in Figure 3, contains about 0.3 weight-% Na_2O and about 1.5 weight-% K_2O. From the OH-concentration point of view, the corresponding so-called $(Na_2O)_{eq}$ is 1.29 weight-%. $(Na_2O)_{eq} = Na_2O + 0.66 \cdot K_2O$.

* The (equivalent) amount of Na_2O is12.9 g/kg cement.
* The mole weight of Na_2O is 62 g/mole.
* The number of mole Na_2O in cement is 12.9/62=0.208 mole/kg cement
* Na_2O is dissociated according to:

$$Na_2O + H_2O = 2Na^+ + 2OH^- \qquad (12)$$

i.e. 1 mole sodium oxide gives 2 moles of OH^-.
* The amount of OH^- in the cement expressed as mole/kg (i.e. the coefficient k) is:
$k = 2 \cdot 0.208 = 0.416$ mole OH^-/kg cement.

In Table 3 the theoretically calculated threshold values from Table 1 are multiplied by the coefficient k=0.416. This gives the free chloride concentration in g/litre. Calculated values are compared with experimentally determined from Figure 3.

Table 3: Calculated and measured threshold values for the free chloride content of water saturated concrete made with Portland cement with the equivalent Na_2O content 1.29 weight-%. The values are based on K=0.6 (the Hausmann criterion)

w_o/c	α	Calculated threshold chloride content in pore water according to Table 1 $\left(Cl^-{}_{free}\right)_{thr}$ g/litre		Measured threshold chloride content in pore water according to Figure 2 $\left(Cl^-{}_{free}\right)_{thr}$ g/litre
		Alt 1 Only capillary water dissolves alkali	Alt 2 and Alt 3 All water dissolves alkali	
0.60	0.75	**29** **(0.82)** [1]	**20** **(0.56)**	20-22 (average 21) (average 0.58)
0.50	0.70	**39** **(1.10)**	**24** **(0.70)**	20-25 (average 23) (average 0.65)
0.40	0.65	**60** **(1.69)**	**32** **(0.90)**	47-53 (average 51) (average 1.44)
0.30	0.50	**85** **(2.39)**	**43** **(1.21)**	Information lacking

1) Values within parentheses are in mole/litre

The values are plotted in Figure 4.The agreement between calculation and measurement is fairly good, particularly when the calculated value of the OH^--concentration is based on the entire water volume. For the lowest water/cement ratio the agreement is best when only capillary pore water is supposed to dissolve alkali.

It must be considered that the data used for soluble alkali in the cement are rather uncertain. Also rather small variations in alkali content affect the calculated threshold value quite much. Furthermore, the selected value K=0.6 is quite uncertain. It must also be noted that the experimental data are uncertain depending on big experimental difficulties associated with these types of measurements.

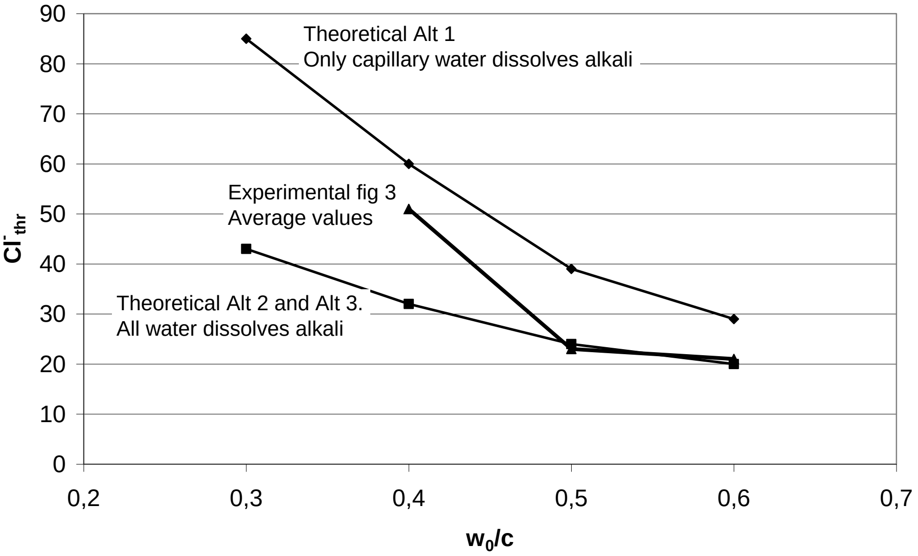

Figure 4: Calculated and measured threshold concentration of free chloride. Data from Table 3.

5.2 LOW-ALKALI CEMENT

A typical low alkali cement like the Swedish Anläggningscement has an Na_2O-equivalent of about 0.5 weight-%. Thus, the coefficient k becomes:
k=2·(5/62)=0.161 mole OH^- per kg cement.

The threshold concentration is obtained by multiplying the values in Table 1 and 3 by the factor 0.161. The coefficient K is assumed to be 0.6.

Example:
Concrete with w/c-ratio 0.40, degree of hydration 0.65. The difference between high-alkali cement (k=0.416) and low alkali cement (k=0.161) is shown in the table below.

Threshold chloride content in pore water $\left(Cl^-_{free}\right)_{thr}$ g/litre			
Low-alkali cement		High-alkali cement	
Alt 1	Alt 2 Alt 3	Alt 1	Alt 2 Alt 3
23 **(0.65)**$^{1)}$	**12** **(0.34)**	**60** **(1.69)**	**32** **(0.90)**

1) Values within parentheses are in mole/litre

The effect of the cement alkalinity is summarized in Figure 5. It is valid for K=0.6.

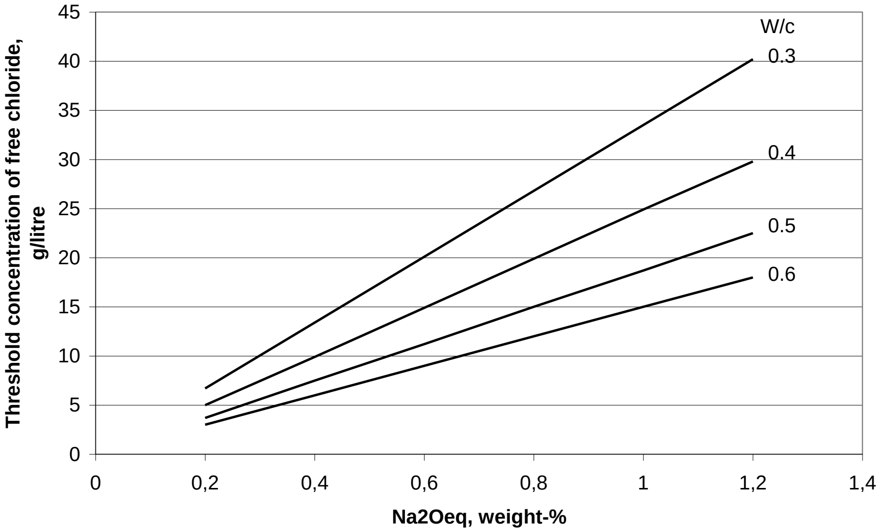

Figure 5: Effect of alkalinity of cement on the threshold concentration of free chloride. The diagram is valid for Alt 2 and Alt 3.

5.3 EFFECT OF THE COEFFICIENT K

The threshold concentration of Cl^--ions required for initiation of corrosion is assumed to be proportional to the concentration of OH^--ions; see Eq. (1). So far the proportionality coefficient K in Eq. (1) has been assumed to be 0.6. This value is based on experiments were ordinary steel has been immersed in chloride solution. The value might be different for steel in concrete due to the following factors: (1) a more complex solution surrounding the steel, (2) a different oxygen concentration, (3) varying electrical potential on different parts of the steel surface. The value might be higher than 0.6, but it might also be lower.

The threshold concentration is directly proportional to the value of K, see Eq. (8) and (9) or (10) and (11). Threshold values can therefore be obtained from Table 1 or 3 by multiplying the table values by the factor K/0.6 and multiplying by the relevant value of the coefficient k.

Example:
High-alkali cement. w/c-ratio 0.40 (k=0.416). Degree of hydration 0.65. **K=0,4**.
The difference between threshold values for K=0.4 and 0.6 is shown in the table below.

Threshold chloride content in pore water $\left(Cl^{-}_{free}\right)_{thr}$ g/litre			
K=0.4		K=0.6	
Alt 1	Alt 2 Alt 3	Alt 1	Alt 2 Alt 3
40 **(1.12)**[1)]	**21** **(0.59)**	**60** **(1.69)**	**32** **(0.90)**

1) Values within parentheses are in mole/litre

6. THRESHOLD VALUE OF *FREE, BOUND* AND *TOTAL* CHLORIDE AS WEIGHT-% OF CEMENT

6.1 Theory

Normally in literature on service life of concrete, the threshold chloride concentration is expressed in terms of the *total* chloride content and not in terms of *free* chloride content. There is a relation between these two values. In the following a theoretical derivation of this relation will be made. It depends on the relation between free and *bound* chloride

Total chloride content is the sum of bound and free chloride:

$$\left(Q_{Cl^{-}total}\right)_C = \left(Q_{Cl^{-}bound}\right)_C + \left(Q_{Cl^{-}free}\right)_C \quad \text{weight-\% of the cement} \qquad (13)$$

The relation between bound chloride content and free chloride content in a concrete is determined by the sorption isotherm for chloride. This relation between the two chloride contents is:

$$\left(Q_{Cl^{-}bound}\right)_C = f\left[\left(Q_{Cl^{-}free}\right)_C\right] \quad \text{weight-\% of the cement} \qquad (14)$$

In the simplest case the relation is linear, i.e.:

$$\left(Q_{Cl^{-}bound}\right)_C = const \cdot \left[\left(Q_{Cl^{-}free}\right)_C\right] \qquad (15)$$

This type of relation was observed by Tuutti (1982).

Often, the isotherm is non-linear. A typical example is seen in Figure 6, Tang (1996). The isotherm is valid for a type of Swedish Portland cement. It must be noted that the unit for bound chloride is different from the unit for free chloride.

The isotherm in Figure 6 can be described by the following equation (a Freundlich isotherm):

$$c_{bound} = a \cdot c_{free}^{\ b} \quad \text{mg/g cement gel} \tag{16}$$

where

a and b are coefficients

c_{bound} is bound chloride expressed as *mg chloride/g cement gel,* i.e. 10^{-3} kg/kg gel

c_{free} is free chloride expressed as *mol chloride ions/litre pore liquid*

For the isotherm in Figure 6, a=13.5 and b=0.41.

$$c_{bound} = 13.5 \cdot c_{free}^{\ 0.41} \quad \text{mg/g cement gel} \tag{16b}$$

Note: the isotherm is only determined for the Cl^--range 0 to1 mole/litre (0-35.5 g/litre). In the following it is assumed that Eq. (16) can also be used for higher concentrations.

Bound and free chloride must be transformed to the unit weight-% of cement.

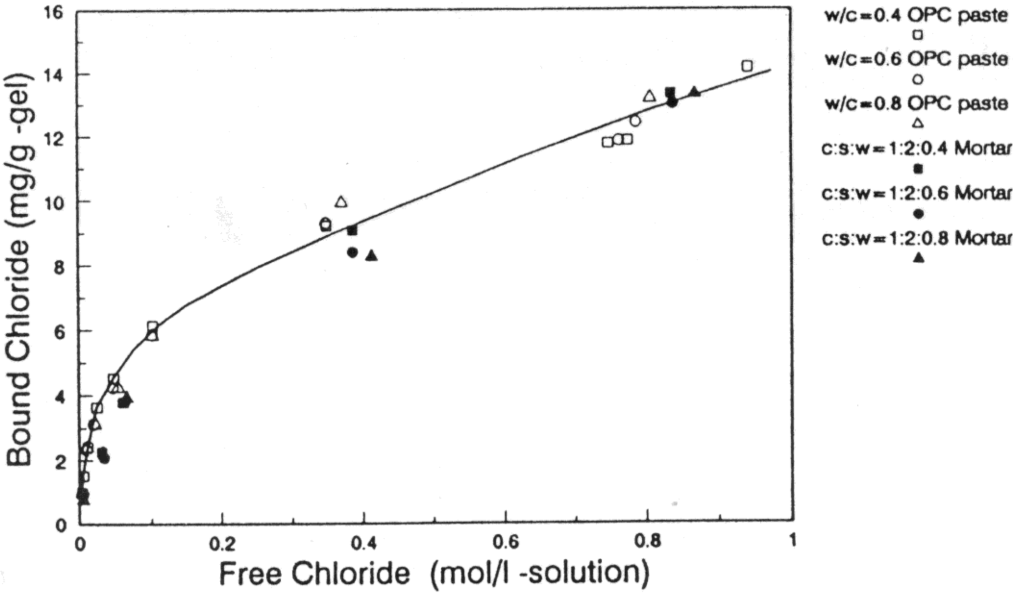

Figure 6: Relation between free and bound chloride in Portland cement paste and Portland cement mortar; Tang (1996).

The weight of cement gel is (by “gel” is in this case meant the sum of all hydration products):

$$Q_{gel} = \alpha \cdot C + w_n = \alpha \cdot C + 0.25 \cdot \alpha \cdot C = 1.25 \cdot \alpha \cdot C \quad \text{kg} \tag{17}$$

or

$$Q_{gel} = 1.25 \cdot \alpha \quad \text{kg/kg cement} \tag{17b}$$

where

α is the degree of hydration

C is the cement weight, kg

w_n is the chemically bound water, kg

The bound chloride in weight-% of cement therefore is:

$$\left(Q_{Cl^- bound}\right)_C = c_{bound}\cdot 10^{-3}\cdot 1.25\cdot\alpha\cdot 100 = c_{bound}\cdot 0.125\cdot\alpha \quad \text{weight-\% of cement} \qquad (18)$$

and

$$\boxed{c_{bound} = \frac{\left(Q_{Cl^- bound}\right)_C}{0.125\cdot\alpha} \quad \text{mg/g cement gel} \qquad (18b)}$$

Example: Concrete with degree of hydration 0.8. The y-axis of Figure 6 (and Eq. (16b)) gives c_{bound}=12.3 mg/g.

According to Eq. (18) the amount of bound chloride is 12.3·0.125·0.8 = 1.23 weight-%.

The free chloride concentration in Figure 6 is the same as $\left[Cl^-{}_{free}\right]$ in Eq. (8) and (9).

$$c_{free} = \left[Cl^-{}_{free}\right] \quad \text{mole/litre} \qquad (19)$$

and

$$\left(c_{free}\right)_{thr} = \left[Cl^-{}_{free}\right]_{thr} \quad \text{mole/litre} \qquad (19b)$$

The threshold amount if free chloride depends on how chloride is dissolved. There are three possibilities, see Figure 1.

Alt 1:

The weight in kg of dissolved chloride at threshold, per litre of water is given by Eq. (10) multiplied by the factor 10^{-3} kg/g.

$$\left(Q_{Cl^- free}\right)_{thr} = \frac{K\cdot k\cdot 35.5\cdot 10^{-3}}{w_0/c - 0.39\cdot\alpha} \quad \text{kg/litre} \qquad (20)$$

The total amount of free chloride is found by multiplying Eq. (20) by the amount of water containing chloride. This is given by Eq. (4). Dividing by the cement weight and multiplying by 100 (%) gives:

$$\left(Q_{Cl^- free}\right)_{C,thr} = \frac{K\cdot k\cdot 35.5\cdot 10^{-3}}{w_0/c - 0.39\cdot\alpha}\cdot\left(w_0/c - 0.39\cdot\alpha\right)\cdot 100 = 3.55\cdot K\cdot k \quad \text{weight-\% of cement} \qquad (21)$$

The threshold concentration (mole/litre) is given by Eq. (8). Thus, according to Eq. (16b) the amount of bound chloride at threshold concentration is:

$$\frac{\left(Q_{Cl^- bound}\right)_{C,thr}}{0.125\cdot\alpha} = a\cdot\left(\frac{K\cdot k}{w_0/c - 0.39\cdot\alpha}\right)^b \qquad (22)$$

or

$$\left(Q_{Cl^- bound}\right)_{C,thr} = 0.125 \cdot \alpha \cdot a \cdot \left(\frac{K \cdot k}{w_0 / c - 0.39 \cdot \alpha} \right)^b \quad \text{weight-\% of cement} \tag{22b}$$

The ***total chloride*** content at threshold concentration as weight-% of cement is:

$$\boxed{\left(Q_{Cl^- total}\right)_{C,thr} = 0.125 \cdot \alpha \cdot a \cdot \left(\frac{K \cdot k}{w_0 / c - 0.39 \cdot \alpha} \right)^b + 3.55 \cdot K \cdot k \quad \text{weight-\% of cement} \qquad (23)}$$

Alt 2:
The weight in kg of dissolved chloride at threshold per litre of water is given by Eq. (11) multiplied by the factor 10^{-3} kg/g.

$$\left(Q_{Cl^- free}\right)_{thr} = \frac{K \cdot k \cdot 35.5 \cdot 10^{-3}}{w_0 / c - 0.19 \cdot \alpha} \quad \text{kg/litre} \tag{24}$$

The total amount of free chloride is found by Eq. (24) multiplied by the amount of water containing chloride. This is given by Eq. (4). Dividing by the cement weight gives:

$$\left(Q_{Cl^- free}\right)_{C,thr} = \frac{K \cdot k \cdot 35.5 \cdot 10^{-3}}{w_0 / c - 0.19 \cdot \alpha} \cdot \left(w_0 / c - 0.19 \cdot \alpha\right) = 3.55 \cdot K \cdot k \quad \text{weight-\% of cement} \tag{21}$$

This is the same as for Alt 1.

The threshold concentration (mole/litre) is given by Eq. (9). Thus, according to Eq. (16b) the amount of bound chloride at threshold concentration is:

$$\frac{\left(Q_{Cl^- bound}\right)_{C,thr}}{0.125 \cdot \alpha} = a \cdot \left(\frac{K \cdot k}{w_0 / c - 0.19 \cdot \alpha} \right)^b \tag{25}$$

or

$$\left(Q_{Cl^- bound}\right)_{C,thr} = 0.125 \cdot \alpha \cdot a \cdot \left(\frac{K \cdot k}{w_0 / c - 0.19 \cdot \alpha} \right)^b \quad \text{weight-\% of cement} \tag{25b}$$

The ***total chloride*** content at threshold concentration as weight-% of cement becomes:

$$\boxed{\left(Q_{Cl^- total}\right)_{C,thr} = 0.125 \cdot \alpha \cdot a \cdot \left(\frac{K \cdot k}{w_0 / c - 0.19 \cdot \alpha} \right)^b + 3.55 \cdot K \cdot k \quad \text{weight-\% of cement} \qquad (26)}$$

Alt 3:
The weight in kg of dissolved chloride at threshold per litre of water is given by Eq. (11) multiplied by the factor 10^{-3} kg/g. The result is Eq. (24) above.

The total amount of free chloride is found by Eq. (24) multiplied by the amount of water containing chloride. This is given by Eq. (5). Dividing by the cement weight and multiplying by 100 (%) gives:

$$\left(Q_{Cl^- \, free}\right)_{C,thr} = \frac{K \cdot k \cdot 35.5 \cdot 10^{-3}}{w_0/c - 0.19 \cdot \alpha} \cdot \left(w_0/c - 0.39 \cdot \alpha\right) \cdot 100 \quad \text{weight-\% of cement} \tag{27}$$

The threshold concentration is given by Eq. (9). Thus, according to Eq. (16b) the amount of bound chloride at threshold concentration is:

$$\frac{\left(Q_{Cl^- \, bound}\right)_{C,thr}}{0.125 \cdot \alpha} = a \cdot \left(\frac{K \cdot k}{w_0/c - 0.19 \cdot \alpha}\right)^b \tag{28}$$

or

$$\left(Q_{Cl^- bound}\right)_{C,thr} = 0.125 \cdot \alpha \cdot a \cdot \left(\frac{K \cdot k}{w_0/c - 0.19 \cdot \alpha}\right)^b \quad \text{weight-\% of cement} \tag{28b}$$

The total chloride content at threshold concentration as weight-% of cement becomes:

$$\boxed{\left(Q_{Cl^- \, total}\right)_{C,thr} = 0.125 \cdot \alpha \cdot a \cdot \left(\frac{K \cdot k}{w_0/c - 0.19 \cdot \alpha}\right)^b + 3.55 \cdot K \cdot k \cdot \frac{w_0/c - 0.39 \cdot \alpha}{w_0/c - 0.19 \cdot \alpha} \quad \text{weight-\%}} \tag{29}$$

6.2 CONCLUSIONS

The threshold concentration of *free* chloride expressed in g/litre or mole/litre of pore solution is determined by 2 coefficients:

1. k determined by the alkalinity of the cement
2. K determined by the relation between the alkalinity of the pore solution and the chloride concentration to start corrosion; Eq. (1).

The threshold value of *total* chloride as weight-% of cement is determined by 4 coefficients, k and K but also two coefficients describing chloride binding:

3. a in Eq. (16)
4. b in Eq. (16)

7. EFFECT OF ALKALINITY OF CEMENT ON THE THRESHOLD CHLORIDE CONTENT

Assuming the Hausmann criterion to be valid (K=0.6) the threshold value of total chloride expressed as weight-% of the cement weight are calculated by Equations (23), (26) and (29). These equations show that there is a linear relation between the coefficient k expressing the alkalinity of cement and the chloride threshold values.

7.1 High alkali Portland cement

The alkalinity of the cement is given by Na_2O_{eq}=1.29 weight-% (the same as the cement in Table 3). This is a typical Swedish ordinary Portland cement.

The coefficient k=0.416, see Eq. (12).

It is assumed that the chloride binding isotherm can be described by Figure 6, i.e. a=13.5, b=0.41.

The calculated threshold values are given in Table 6.

Table 6: The threshold concentration of chloride as weight-% of cement in saturated portland cement concrete. The degree of hydration selected is normal for concrete that is a couple of months old. The cement alkalinity Na_2O_{eq}=1.29 %. The values are based on the Hausmann criterion, K=0.6. Isotherm according to Figure 6.

w_o/c	α	Threshold chloride concentration (weight-% of cement)								
		Alt 1			Alt 2			Alt 3		
		free	bound	**total**	free	bound	**total**	free	bound	**total**
0.60	0.75	0.89	1.16	**2.05**	0.89	0.99	**1.88**	0.60	0.99	**1.59**
0.50	0.70		1.23	**2.12**		1.01	**1.90**	0.55	1.01	**1.56**
0.40	0.65		1.36	**2.25**		1.05	**1.94**	0.47	1.05	**1.52**
0.30	0.50		1.20	**2.09**		0.92	**1.91**	0.46	0.92	**1.38**
Average value (std. dev.)				**2.1** **(0.09)**			**1.9** **(0.03)**			**1.5** **(0.09)**

The effect of the manner in which chloride and alkali is dissolved is rather big. As said above in paragraph 2, Alt 3 seems to be the most plausible alternative.

The threshold of total chloride content of mature concrete varies within the span 1.4-1.6 % for Alt 1. The other two alternatives give higher values; about 1.9 to 2.2%. Thus, for each alternative the variation in threshold concentration is quite small.

7.2 Low alkali Portland cement

A typical low alkali cement like the Swedish Anläggningscement has the Na_2O-equivalent about 0.5 weight-% =5g/kg cement.

The coefficient k=2·(5/62) =0.161; see paragraph 5.2.

The Hausmann criterion (K=0.6) is supposed to be valid. The binding isotherm is described by Figure 6.

The values for free chloride are based on the values in Table 6 multiplied by the factor 0.161/0.416=0.39. The values for bound chloride are based on the values in Table 6 multiplied by the factor $(0.161/0.416)^{0.41}$=0.68.

The threshold concentration is listed in Table 7.

For Alt 3 the threshold of total chloride content of mature concrete is about 0.6 weight-% for all w/c-ratios. For the other two alternatives lies within the span 0.7-0.8 weight-%.

The calculation indicates that corrosion will start at lower chloride content in a concrete with low alkali cement, provided that the binding capacity of chloride is not increased, viz. it must be noted tat all data in Tables 6 and 7 are based on the same binding isotherm. If low alkali cement is able to bind more chloride, the negative effect regarding threshold concentration will be compensated for more or less completely; see paragraph 9.

Table 7: The threshold concentration of chloride as weight-% of cement in saturated portland cement concrete. The degree of hydration selected is normal for concrete that is a couple of months old. The cement alkalinity Na_2O_{eq}=0.5 %. The values are based on the Hausmann criterion, K=0.6. Isotherm according to Figure 6.

w_o/c	α	Threshold chloride concentration (weight-% of cement)								
		Alt 1			Alt 2			Alt 3		
		free	bound	**total**	free	bound	**total**	free	bound	**total**
0.60	0.75	0.35	0.79	**1.14**	0.35	0.67	**1.02**	0.23	0.67	**0.90**
0.50	0.70		0.83	**1.18**		0.68	**1.03**	0.21	0.68	**0.89**
0.40	0.65		0.92	**1.27**		0.71	**1.06**	0.18	0.71	**0.89**
0.30	0.50		0.81	**1.16**		0.62	**0.97**	0.18	0.62	**0.80**
Average value (Std. dev.)				**1.19** **(0.05)**			**1.02** **(0.04)**			**0.87** **(0.05)**

7.3 Conclusions

1. *The calculations above show that the assumption that there exists a critical free chloride concentration –Eq.(1)- theoretically leads to a threshold chloride concentration expressed as weight-% of cement that is almost constant irrespectively of the composition of the concrete as long as the same cement type is used. It only depends on how alkali is dissolved in the pore system, Alt 3 giving the lowest threshold concentration.*

2. *For all three alternatives of dissolution of chloride and alkali, the effect of the water/cement ratio on the threshold chloride content is small when this is expressed in terms of weight-% of cement. However, when the threshold of free chloride is expressed in terms of chloride concentration in pore water the effect of w/c-ratio is big; see Table 3.*

8. EFFECT OF THE CRITICAL $[Cl^-]/[OH^-]$-RATIO ON THE THRESHOLD CHLORIDE CONTENT

Equations (23), (26) and (29) show a linear relation between the coefficient K in Eq. (1) and the threshold concentration. Thus, the threshold concentration for another value of K than 0.6 is found by multiplying the vales in Table 6 or 7 by the factor K/0.6, assuming the isotherm in Figure 6 is still valid.

Example:

- The coefficient K is 0.4. Then, the threshold concentrations of free chloride in Table 6 and 7 shall be multiplied by the factor 0.4/0.6=0.67. The threshold concentration of bound chloride in Tables 6 and 7 shall be multiplied by the factor $(0.4/0.6)^{0.41}$=0.85.
- Concrete with w/c-ratio 0.40 and degree of hydration 0.65.
- Dissolution of chloride and alkali defined by *Alternative 3.*
- The binding isotherm is given by Figure 6.

The threshold chloride content for this concrete expressed in weight-% of cement is shown in Table 8

Table 8: The critical threshold value of chloride for different values of the critical [Cl⁻]/[OH⁻] ratio. Water-cement ratio 0.40. Alt 3. Values for K=0.6 taken from Tables 6 and 7.

Cement type	Low critical OH⁻concentration K=0.4 Weight-% of cement			High critical OH⁻concentration K=0.6 Weight-% of cement		
	free	bound	total	free	bound	total
High alkali k=0.416	0.31	0.89	**1.20**	0.47	1.05	**1.52**
Low alkali k=0.161	0.12	0.60	**0.72**	0.18	0.71	**0.89**

The effect of K is smaller than what might have been expected. A reduction of K by 50% (from 0.6 to 0.4) only causes a decrease in the threshold chloride concentration by about 20%.The reason is that the bound chloride is less than directly proportional the value of K.

9. EFFECT OF THE CHLORIDE BINDING CAPACITY ON THE THRESHOLD CHLORIDE CONTENT

The chloride binding capacity depends on the chemical composition of the cement. Binding is both chemical and physical.

Portland cement paste is composed of four major components.

1. Hydrated calcium-silicate gel (C-S-H).
2. Calcium hydroxide
3. AFm-phase (monosulfate)
4. AFt-phase (ettringite)

The first phase is formed at hydration of the calcium-silicate in cement. The second phase is primarily formed at hydration of calcium-silicate, but also at hydration of aluminate in cement. The last two phases are formed at hydration of the aluminate and ferrite in cement.

Hirao et al (2005) have shown experimentally that the calcium hydroxide and the Aft-phase do not bind chloride. AFm on the other hand binds chloride chemically primarily by formation of a compound called Friedel´s salt. The binding isotherm of chloride on AFm is of a Freundlich type which is described by Eq. (16). Hirao et al (2005) give the following isotherm:

$$c_{bound,AFm} = 0.4566 \cdot c_{free}^{\ 0.6016} \tag{16b}$$

where

$c_{bound,AFm}$ is expressed in the unit (mole bound Cl⁻/mole AFm). (The mole weight of AFm ($3CaO\cdot Al_2O_3\cdot CaSO_4\cdot 12H_2O$) is 622 g/mole.)

c_{free} is expressed in the unit (mole Cl⁻/litre)

The total amount of bound chloride depends on the amount of AFm in cement paste. This is different for different types of cement.

Pure C-S-H gel ($Ca(OH)_2$ not included) binds chloride physically. Experiments by Hirao (2005) at al indicate that the binding isotherm is of a Langmuir type:

$$c_{bound,CSH} = 0.61 \cdot \frac{2.65 \cdot c_{free}}{1 + 2.65 \cdot c_{free}} \tag{30}$$

where
$c_{bound,CSH}$ is expressed in the unit (mmole bound chloride/g C-S-H gel
c_{free} is expressed in the unit (mole chloride/litre)

According to Eq. (30) binding is saturated when c_{bound}=0.61.

When $Ca(OH)_2$ is included in "gel", Eq (30) is changed to, Hirao et al (2005):

$$c_{bound,CSH} = 0.47 \cdot \frac{2.65 \cdot c_{free}}{1 + 2.65 \cdot c_{free}} \tag{30b}$$

Comparison of the two equations (30) and (30b) shows that 1 kg of fully hydrated cement produces 0.30 kg $Ca(OH)_2$.

Eq. (30b) gives the bound chloride content 0.34 mmole/g gel, or 12 mg/g, when the outer chloride concentration is 1 mmole/litre. This is somewhat smaller binding than obtained from Figure 6. However, in this figure also the AFm and Aft phases are included in the definition of gel. This can explain the higher value.

Since the amount of AFm and AFt is different for different cement types, the sorption isotherm will be different. It is, however, assumed that total binding can always be described by a Freundlich type of isotherm for all cements; Eq. (16). The coefficients a and b will however be somewhat different for different types of cement.

It is assumed that the coefficient b is the same as for Figure 6, i.e. b=0.41.

Then, the threshold concentration of bound chloride as weight-% of cement can be calculated by Equations (22b), (25b) and (28b) with the relevant value of b inserted.

Let us assume that binding is only 50% of that shown in Figure 6. Then, the coefficient a becomes:

a=13.5/2=6.75.

For a high-alkali cement with Na_2O_{eq}=1.29 (k=0.416) and K=0.6 (the Hausmann criterion) the threshold concentration can be calculated from the values in Table 6. The value for critical free chloride is unchanged. The value for bound chloride is multiplied by the factor 0.5. Calculated threshold concentrations for this cement is shown in Table 9.

Table 9: The threshold concentration of chloride as weight-% of cement in saturated portland cement concrete. The degree of hydration selected is normal for concrete that is a couple of months old. The cement alkalinity Na_2O_{eq}=1.29 %. The values are based on the Hausmann criterion, K=0.6. Isotherm according to Figure 6 with bound chloride divided by the factor 2.

w_o/c	α	Threshold chloride concentration (weight-% of cement)								
		Alt 1 $^{1)}$			Alt 2 $^{2)}$			Alt 3 ^{3})		
		free	bound	**total**	free	bound	**total**	free	bound	**total**
0.60	0.75	0.89	0.58	**1.47**	0.89	0.50	**1.39**	0.60	0.50	**1.10**
0.50	0.70		0.62	**1.51**		0.51	**1.40**	0.55	0.51	**1.06**
0.40	0.65		0.68	**1.57**		0.53	**1.42**	0.47	0.53	**1.00**
0.30	0.50		0.60	**1.49**		0.46	**1.35**	0.46	0.46	**0.92**
Average value (std. dev.)				**1.5** **(0.04)**			**1.4** **(0.03)**			**1.0** **(0.07)**

1) Only capillary water dissolves alkali and chloride
2) All pore water dissolves alkali and chloride
3) All water dissolves alkali. Only capillary water dissolves chloride

10. EFFECT OF CONCRETE AGE ON THE THRESHOLD CHLORIDE CONTENT

Effect of concrete age on the threshold chloride concentration and content is calculated by equations above by inserting the relevant value of degree of hydration.

10.1 Threshold concentration of free chloride in pore water

Alt 3 for dissolution of alkali and chloride is used; i.e. Equation (11) is used.

An example of the effect of degree of hydration is shown in Table 10 for the water/cement ratio 0.40. As before, in Table 3, 6 and 8, the coefficient K is 0.6 (the Hausmann criterion) and the coefficient k is 0.417 (high-alkali cement).

The threshold concentration of free chloride expressed in kg/litre is shown in Table 10.

Table 10: Threshold concentration of free chloride as function of the degree of hydration. w/c-ratio 0.40. K=0.6 and k=0.416. Alt 3 for dissolution.

Degree of hydration α	The threshold concentration $\left(Cl_{free}\right)_{thr}$ (g/litre pore water)	
	Alt 1	Alt 2 and Alt 3
0.40	**36.4**	**27.4**
0.60	**53.5**	**31.1**
0.80	**100.9**	**35.8**
1.00	**888.2**	**42.2**

The threshold concentration increases with increased concrete age. This is particularly evident when it is assumed that chloride and alkali is only dissolved in capillary water, Alt 1. In this case the capillary pore volume is very low in cement paste with w/c-ratio 0.4 when the degree of hydration is high. Thus, the OH^--concentration becomes extremely high at full hydration in a concrete with water/cement ratio 0.40. Therefore, very high chloride concentration is needed to initiate corrosion. However, as said above, Alt 3 is the most plausible alternative.

10.2 Threshold value of chloride in weight-% of cement

Equations in paragraph 6.1 are used; i.e. Eq. (23), (26), (29).

As example the same concrete as above is studied, i.e. w/c=0.40, K=0.6, k=0.417. Chloride binding is described by Figure 6.

The threshold values of free, bound and total chloride expressed in weight-% of cement are shown in Table 11.

Table 11: Threshold values as weight-% of cement of free, bound ant total chloride as function of the degree of hydration.
w/c-ratio 0.40. K=0.6 and k=0.416. Chloride binding according to Figure 6.

α	Threshold chloride concentration (weight-% of cement)								
	Alt 1			Alt 2			Alt 3		
	free	bound	**total**	free	bound	**total**	free	bound	**total**
0.40	0.89	0.68	**1.57**	0.89	0.61	**1.50**	0.67	0.61	**1.28**
0.60		1.20	**2.09**		0.96	**1.85**	0.51	0.96	**1.47**
0.80		2.07	**2.96**		1.35	**2.24**	0.31	1.35	**1.66**
1.00		6.31	**7.20**		1.81	**2.70**	0.04	1,81	**1.85**

The threshold value of free chloride expressed as weigh-% of the cement is independent of age for alternatives 1 and 2. In this case, both the alkali and the chloride concentration changes to the same extent when concrete age is increased, at the same time as chloride binding has no influence. For alternative 3 the threshold value of free chloride decreases with concrete age. The reason is that the (aggressive) chloride concentration increases more with degree of hydration than the (protective) alkaline concentration.

The bound chloride increases with increased degree of hydration for all alternatives which depends on the fact that more gel, which is the component binding chloride, is formed.

11. EFFECT OF LIMESTONE IN CEMENT ON THE THRESHOLD CHLORIDE CONTENT

Cement containing limestone filler will have reduced alkalinity. Therefore the threshold value of free chloride will be reduced.

It is assumed that filler does not influence the pore structure. This is determined by the Portland part of the cement. Therefore, one can define an *effective water-cement ratio* defined:

$$(w_0/c)_{eff} = w_0/PC = \frac{w_0/c}{1-g} \tag{31}$$

where

PC is the amount of Portland component in concrete (kg)
w_0 is the amount of mixing water in concrete (kg)
c is the amount of cement in concrete (including limestone) (kg)
g is the weight fraction of limestone filler in the cement (-) (the density of limestone is supposed to be the same as the density of Portland cement). (g=(c-PC)/c)

11.1 Threshold concentration of free chloride in pore water

Equations (10) and (11) can be used provided w_o/c in these equations is replaced by the effective water-cement ratio. The revised equations are:

Alt 1:

$$\left(Cl^{-}{}_{free}\right)_{thr} = \frac{K \cdot k \cdot 35.5}{\frac{w_0/c}{1-g} - 0.39 \cdot \alpha} \quad \text{g/litre} \tag{10a}$$

Alt 2 and 3:

$$\left(Cl^{-}{}_{free}\right)_{thr} = \frac{K \cdot k \cdot 35.5}{\frac{w_0/c}{1-g} - 0.19 \cdot \alpha} \quad \text{g/litre} \tag{11a}$$

These equations are applied to the same portland clinker as that used in the calculation behind Table 4 (k=0.417). The Hausmann criterion is used (K=0.6). The filler content g is supposed to be 20% (the highest value accepted according to the cement standard). The calculated threshold concentrations are shown in Table 12.

Table 12: Calculated threshold values for the free chloride content of water saturated concrete made with Portland cement mixed with 20% limestone filler. Na_2O content of the Portland component is 1.29 weight-%. The values are based on K=0.6 (the Hausmann criterion)

w_o/c	α	Calculated threshold chloride content in pore water $\left(Cl^{-}{}_{free}\right)_{thr}$ g/litre	
		Alt 1	Alt 2 and Alt 3
0.60	0.75	**19.4**	**14.6**
0.50	0.70	**25.2**	**18.0**
0.40	0.65	**36.0**	**23.6**
0.30	0.50	**49.3**	**31.7**

These values can be directly compared with the calculated values in Table 4, which are valid for pure Portland cement. The relation between the threshold values is shown in Table 13.

Table 13: Threshold concentration of free chloride content. Portland cement compared with filler cement containing 20% filler.

w_o/c	Threshold concentration of free chloride filler cement/Portland cement	
	Alt 1	Alt 2 and Alt 3
0.60	0.67	0.73
0.50	0.65	0.75
0.40	0.60	0.74
0.30	0.58	0.74
Average	**0.63**	**0.74**

Thus, the reduction in threshold chloride content when inert filler is mixed into the concrete is bigger than the fraction of filler.

11.2 Threshold value of chloride in weight-% of cement

The threshold concentration of total chloride in weight-% of cement is calculated by Eq. (23), Eq. (26) or Eq. (29). The equations have to be modified to take the filler into consideration.

The amount of cement gel is reduced, since limestone filler is non-reactive. Eq. (17) is changed to:

$$Q_{gel} = 1.25 \cdot \alpha \cdot (1-g) \quad \text{kg/kg cement} \qquad (17c)$$

Thus, Eq. (18b) describing the amount of bound chloride is changed to:

$$\left(Q_{Cl^- bound}\right)_C = c_{bound} \cdot 10^{-3} \cdot 1.25 \cdot \alpha \cdot (1-g) \cdot 100 = c_{bound} \cdot 0.125 \cdot \alpha \cdot (1-g) \quad \text{weight-\%} \qquad (18c)$$

The water cement ratio in the three equations is changed for the effective water cement ratio; Eq. (31).

The threshold chloride content becomes for the three alternatives:

Alt 1:

$$\left(Q_{Cl^- total}\right)_{C,thr} = 0.125 \cdot \alpha \cdot (1-g) \cdot a \cdot \left(\frac{K \cdot k}{\frac{w_0/c}{1-g} - 0.39 \cdot \alpha} \right)^b + 3.55 \cdot K \cdot k \quad \text{weight-\%} \qquad (23a)$$

Alt 2:

$$\left(Q_{Cl^- total}\right)_{C,thr} = 0.125 \cdot \alpha \cdot (1-g) \cdot a \cdot \left(\frac{K \cdot k}{\frac{w_0/c}{1-g} - 0.19 \cdot \alpha} \right)^b + 3.55 \cdot K \cdot k \quad \text{weight-\%} \qquad (26a)$$

Alt 3:

$$\left(Q_{Cl^- total}\right)_{C,thr} = 0.125 \cdot \alpha \cdot (1-g) \cdot a \cdot \left(\frac{K \cdot k}{\frac{w_0/c}{1-g} - 0.19 \cdot \alpha} \right)^b + 3.55 \cdot K \cdot k \cdot \frac{\frac{w_0/c}{1-g} - 0.39 \cdot \alpha}{\frac{w_0/c}{1-g} - 0.19 \cdot \alpha} \quad \% \qquad (29a)$$

These equations are applied to the same portland clinker as that used in the calculation behind Table 6 (k=0.417). The Hausmann criterion is used (K=0.6). The filler content g is supposed to be 20%. Chloride binding is described by Figure 6. The calculated threshold concentrations are shown in Table 14.

Table 14: Calculated threshold values for the free chloride content of water saturated concrete made with Portland cement mixed with 20% limestone filler. Na_2O *content of the Portland component is 1.29 weight-%. The values are based on K=0.6 (the Hausmann criterion) and chloride binding according to Figure 6.*

w_o/c	α	Calculated total chloride threshold content as weight-% of cement $\left(Q_{Cl^- total}\right)_{C,thr}$		
		Alt 1	Alt 2	Alt 3
0.60	0.75	1.68	1.59	1.37
0.50	0.70	1.71	1.60	1.35
0.40	0.65	1.77	1.63	1.32
0.30	0.50	1.66	1.53	1.22
Average		**1.70**	**1.59**	**1.32**

The values can be directly compared with the calculated values in Table 6, which are valid for pure Portland cement. The relation between the threshold values is shown in Table 15.

Table 15: Threshold concentration of free chloride content. Portland cement compared with filler cement containing 20% filler.

w_o/c	Threshold amount of total chloride fillercement/portlandcement		
	Alt 1	Alt 2	Alt 3
0.60	0.82	0.84	0.86
0.50	0.81	0.84	0.87
0.40	0.79	0.84	0.87
0.30	0.79	0.80	0.88
Average	**0.80**	**0.83**	**0.87**

The total chloride threshold is markedly reduced when the cement contains inert filler. Comparison with Table 12 shows, however, that the effect of filler on the threshold in terms of weight-% of cement is somewhat smaller than the reduction in terms of chloride concentration in pore water.

12. EFFECT OF MINERAL ADMIXTURES ON THE THRESHOLD CHLORIDE CONTENT

Reactive mineral admixtures (silica fume, granulated blast furnace slag, fly ash) reduce the alkalinity of the pore solution. Examples are shown in Figure 7 (silica fume) and Figure 8 (blast furnace slag, silica fume, and Portland cement).

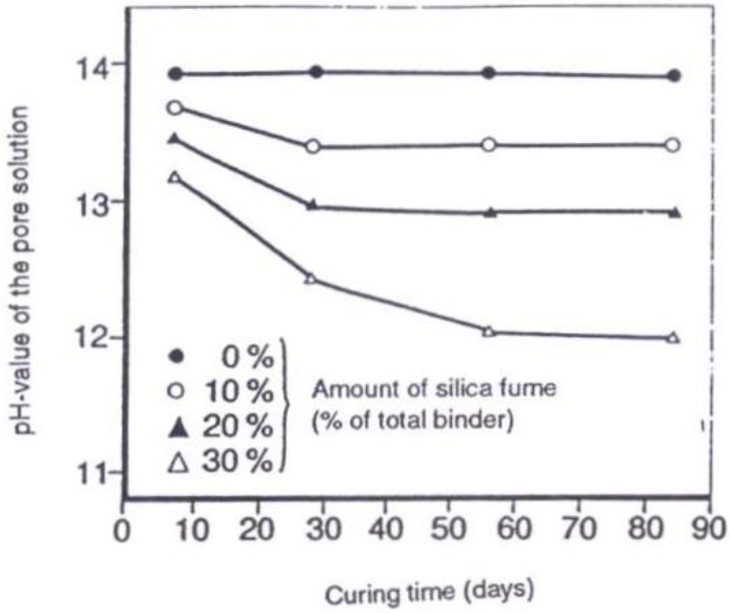

Fig 7: Observed pH-values of pore solution in cement paste mixed with different amount of silica fume, Page & Vennesland (1983). w/c=0.50.

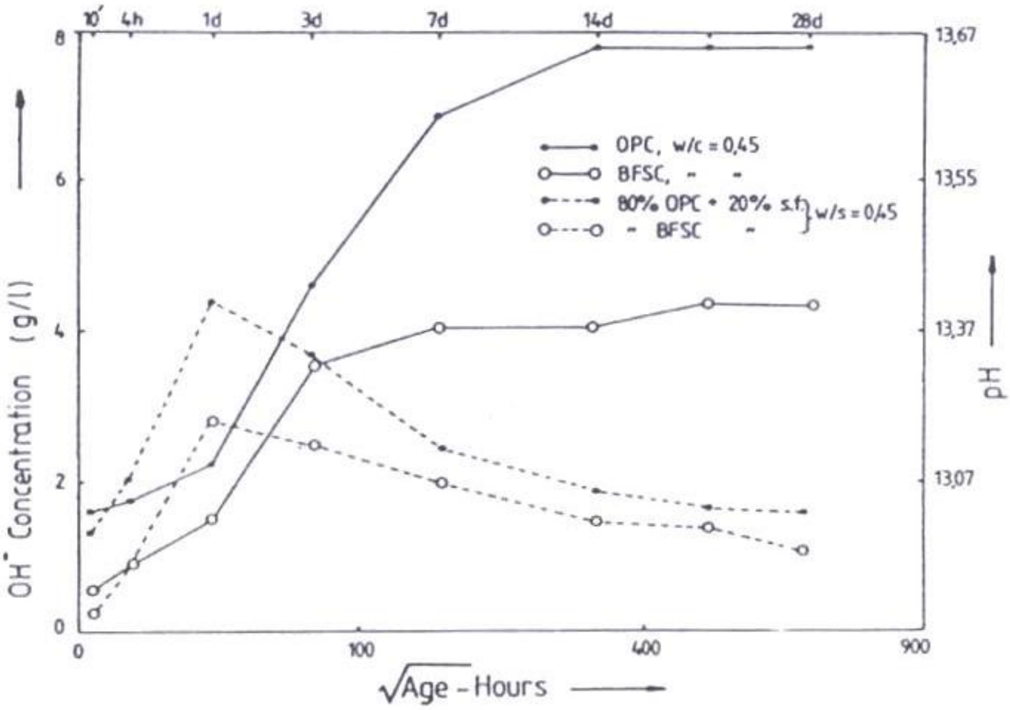

Fig 8: Measurements of the pH-value of pore solution in concrete produced with Portland cement (OPC) or slag cement with 70% slag (BFSC). Both types of concretes were produced with or without 20% silica fume, Bijen (1989). w/c=045.

12.1 Threshold concentration of free chloride in pore water

The OH^--concentration in the pore solution is calculated from the pH-value:

$$\left[OH^-\right] = 10^{pH-14} \quad \text{mole/litre} \tag{32}$$

The threshold concentration is; Eq. (1):

$$\left[Cl^-\right]_{thr} = K \cdot 10^{pH-14} \quad \text{mole/litre} \tag{33}$$

where K=0.6 according to Hausmann.

The threshold concentration expressed in the unit g/litre is obtained by:

$$\left(Cl^-{}_{free}\right)_{thr} = 35.5 \cdot K \cdot 10^{pH-14} \ \text{g/litre} \tag{34}$$

pH of the pore solution can be determined experimentally on water squeezed out from the concrete. Examples of the application of this technique are given in Tuutti (1982).

In the following, pH-values from Figure 7 and 8 are inserted in eq. (34).

Silica fume
Threshold values of free chloride for cement paste with silica fume (from Fig. 7) are shown in Table 16. The Hausmann criterion (K=0.6) is assumed to be valid.

Table 16: Threshold value of free chloride in cement paste and concrete containing silica fume. Long-term values. K=0.6.

	Amount of silica fume %	pH	Threshold value g/litre
Cement paste Fig. 7	0	14.0	21.3
	10	13.4	5.4
	20	13.0	2.1
	30	12.0	0.2
Concrete Fig. 8	Amount of silica fume %		
	0	13.66	9.7
	20	12.97	2.0

The threshold value for pure cement in Fig. 8 is lower than calculated above in paragraph 5 for high and low alkali cements. This might depend on errors in determination of the pH-value. Even very small errors in measured pH of squeezed-out pore water give very big effect in alkali content.

The calculation shows that silica fume will have a negative effect with regard to the threshold concentration of chloride in pore water. Already 10% silica fume in cement paste reduces the threshold concentration by 75%. 20% silica fume in concrete reduces the threshold value by 80%.

Blast furnace slag with or without silica fume

The threshold values of free chloride for concrete with blast furnace slag concrete compared with OPC concrete (from Fig. 8) are shown in Table 17. The Hausmann criterion (K=0.6) is assumed to be valid.

Table 17: *Threshold value of free chloride in concrete containing blast furnace slag with or without silica fume. K=0.6.*

	Amount of silica fume %	pH	Threshold value g/litre
Slag cement 70% slag	0	13.41	5.5
	20	12.79	1.3

The slag cement concrete has lower threshold value than the pure Portland cement concrete; 5.5 g/litre versus 9.7 g/litre. Thus, the threshold value is reduced by 45%.

Use of silica fume in slag cement concrete further lowers the threshold value.

12.2 Threshold value of chloride in weight-% of cement

Only alternative 3 is considered below. The effect of the other two alternatives can be easily calculated in similar manner.

Free chloride

The total amount of free chloride at threshold concentration is obtained by the following equation:

$$\left(Q_{Cl^-free}\right)_{thr} = \left(Cl^-{}_{free}\right)_{thr} \cdot 10^{-3} \cdot V_{P,Cl} \quad \text{kg} \tag{35}$$

where $V_{P,Cl}$ is the capillary pore volume in litres. By “capillary pore volume” is now meant pore volume able to contain chloride ions.

Dividing by the cement content C (kg) and multiplying by 100 gives the total amount of free chloride in weight-% of the concrete:

$$\left(Q_{Cl^-free}\right)_{C,thr} = \frac{\left(Cl^-{}_{free}\right)_{thr} \cdot 10^{-1} \cdot V_{P,Cl}}{C} = \frac{3.55 \cdot K \cdot 10^{pH-14} \cdot V_{P,Cl}}{C} \quad \text{weight-\% of cement} \tag{36}$$

Where C is the sum of the amount of Portland cement and mineral admixture.

If mineral admixtures do not affect the porosity, which is the case at moderate contents, $V_{P,Cl}$ is given by Eq. (5). Therefore, Eq. (35) is transformed to:

$$\left(Q_{Cl^-free}\right)_{thr} = \left(Cl^-{}_{free}\right)_{thr} \cdot 10^{-3} \cdot C \cdot \left(w_0/c - 0.39 \cdot \alpha\right) \quad \text{kg/m}^3 \tag{36a}$$

Inserting Eq. (34), dividing by C and multiplying by 100 (to give %) gives:

$$\left(Q_{Cl^-free}\right)_{C,thr} = 3.55 \cdot K \cdot 10^{pH-14} \cdot \left(w_0/c - 0.39 \cdot \alpha\right) \quad \text{weight \% of cement} \tag{37}$$

Principally, this is the same equation as Eq. (27). The difference is that in this equation the threshold concentration is based on calculation, while it is based on measurement in Eq. (37).

Bound chloride

The binding isotherm for concrete with mineral admixtures is different from concrete with Portland cement. The higher the amount of admixture the bigger is the difference. It is assumed, however, the binding isotherm is of the Freundlich type described by Eq. (16). c_{bound} in this equation is bound chloride expressed in terms of *mg gel/g hydration product.* This depends on the type of mineral admixture and on the degree of reaction of this. It can be described:

$$Q_{hydrationproduct} = h \cdot \beta \cdot C \quad \text{kg} \tag{38}$$

where
h is the amount of hydration product formed per kg hydrated cement, kg/kg
β is the degree of reaction of the “binder” (cement+admixture) (0≤h≤1)
C is the amount of cement (Portland+mineral admixture), kg

This equation is of the same type as Eq. (17). For pure Portland cement, h=1.25.

The total amount of bound chloride in weight-% of the cement becomes, cf. Eq. (18):

$$\left(Q_{Cl^- bound}\right)_C = c_{bound} \cdot 10^{-3} \cdot h \cdot \beta \cdot 100 \quad \text{weight-\% of cement} \tag{39}$$

The threshold free concentration in mole/litre is given by Eq. (33). Inserting this in Eq. (16) gives:

$$c_{bound} = a \cdot \left(K \cdot 10^{pH-14}\right)^b \tag{40}$$

Inserting this in Eq. (39) gives the total amount of bound chloride in weight-% of cement:

$$\left(Q_{Cl^- bound}\right)_C = 10^{-1} \cdot h \cdot \beta \cdot a \cdot \left(K \cdot 10^{pH-14)}\right)^b \tag{41}$$

For Portland cement Eq. (41) is equivalent to Eq. (28b).

Total chloride

The threshold of total chloride as weight-% of cement becomes:

$$\boxed{\left(Q_{Cl^- total}\right)_{C,thr} = 10^{-1} \cdot h \cdot \beta \cdot a \cdot \left(K \cdot 10^{pH-14}\right)^b + \frac{3.55 \cdot K \cdot 10^{pH-14} \cdot V_{P,Cl}}{C} \qquad (42)}$$

For small amount of mineral admixture the capillary pore volume can be described by Eq. (4). Eq. (42) is changed to:

$$\left(Q_{Cl^- total}\right)_{C,thr} = 10^{-1} \cdot h \cdot \beta \cdot a \cdot \left(K \cdot 10^{pH-14}\right)^b + 3.55 \cdot K \cdot 10^{pH-14} \cdot \left(w_0 / c - 0.39 \cdot \alpha\right) \tag{42a}$$

For pure Portland cement this equation is transformed to Eq. (29).

Eq. (42a) is applied to concrete with silica fume. pH from Fig 7 and Table 15 is used (the silica content limited to 20%). The Hausmann criterion (K=0.6) is supposed to be valid. Chloride binding is supposed to be described by Figure 6; i.e. a=13.5, b=0.41. h=1.25 (the same as for Portland cement). The capillary porosity is supposed to be the same as for pure Portland cement which means that β is replaced by the degree of hydration α which is supposed to be 0.70. The water-cement ratio is supposed to be 0.50.

Under these conditions, threshold values in Table 18 are valid.

Table 18: Threshold values of free, bound and total chloride for the cement pastes with silica fume. pH from Figure 7. Alt 3 for dissolution.

Amount of silica fume %	Threshold concentration weight-% of cement		
	Alt. 3		
	Free	Bound	Total
0	0.48	0.96	1.44
10	0.12	0.54	0.66
20	0.05	0.30	0.35

Theoretically, 10% silica fume reduces the threshold value of total chloride by about 50%. Normally only 5% silica fume is used. Interpolation of the values in Table 17 indicates that this would cause a reduction in the threshold concentration by about 25%.

13. EFFECT OF LEACHING OF ALKALI ON THE THRESHOLD CHLORIDE CONTENT

A method to calculate the rate of leaching is presented in APPENDIX 2.

13.1 Threshold concentration of free chloride in pore water

When concrete is stored in water (salt or pure) alkali is leached out which will decrease the threshold concentration.

13.1.1 Total leaching

When all alkali (NaOH and KOH) has been leached out in concrete surrounding the reinforcement bar the pore water surrounding this is a saturated solution of $Ca(OH)_2$. Its pH-value is 12.3.

The threshold chloride concentration is:

$$\left[Cl^-\right]_{thr} = K \cdot 10^{12.3-14} = 0.02 \cdot K \quad \text{mole/litre} \qquad (43)$$

or

$$\boxed{\left(Cl^-{}_{free}\right)_{thr} = 35.5 \cdot 0.02 \cdot K = 0.71 \cdot K \quad \text{g/litre} \qquad (44)}$$

For K=0.6 (the Hausmann criterion) the free chloride content for all w/c ratios is:

$$\left(Cl^-{}_{free}\right)_{thr} = 0.71 \cdot 0.6 = 0.43 \quad \text{g/litre} \qquad (44a)$$

This is a very low value compared with the values for non-leached concrete, see Tables 3 and 4.

13.1.2 Partial leaching

When only part of the alkali have been leached out the pH-value will be higher than 12.3. The threshold concentration becomes, see Eq. (43):

$$\left[Cl^-\right]_{thr} = K \cdot 10^{pH-14} = K \cdot \left[OH^-\right] \quad \text{mole/litre} \tag{43a}$$

or

$$\left(Cl^-{}_{free}\right)_{thr} = 35.5 \cdot K \cdot 10^{pH-14} = 35.5 \cdot K \cdot \left[OH^-\right] \quad \text{mole/litre} \tag{45}$$

Where the pH-value and OH^--concentration depends on the remaining amount of Na^+ and K^+-ions.

13.2 Threshold value of chloride in weight-% of cement – total leaching

Only Portland cement is considered.

Only total leaching is considered. When leaching is not complete the same equations can be used by exchanging the coefficient 0.71 for the expression $35.5 \cdot 10^{pH-14}$, or $35.5 \cdot \left[OH^-\right]$.

Free chloride

The total amount of free chloride at threshold concentration is obtained by the following equation:

$$\left(Q_{Cl^- free}\right)_{thr} = \left(Cl^-{}_{free}\right)_{thr} \cdot 10^{-3} \cdot V_{P,Cl} = 0.71 \cdot K \cdot 10^{-3} \cdot V_{P,Cl} \qquad \text{kg} \tag{46}$$

where $V_{P,Cl}$ is the volume of pore water able to dissolve chloride (litres).

Alt 1 and Alt 3:

$V_{P,Cl}$ is equal to the capillary pore volume, Eq. (4). Inserting this in Eq. (46), dividing by C, and multiplying by 100 (for %) gives the free chloride content in weight-% of cement:

$$\left(Q_{Cl^- free}\right)_{C,thr} = 0.71 \cdot K \cdot 10^{-1} \cdot \left(w_0 / c - 0.39 \cdot \alpha\right) \quad \text{weight-\% of cement} \tag{47}$$

Alt 2:

$V_{P,Cl}$ is equal to the total porosity, Eq. (5). Inserting this in Eq. (46), dividing by C, and multiplying by 100 gives:

$$\left(Q_{Cl^- free}\right)_{C,thr} = 0.71 \cdot K \cdot 10^{-1} \cdot \left(w_0 / c - 0.19 \cdot \alpha\right) \quad \text{weight-\% of cement} \tag{48}$$

Bound chloride

The bound chloride is described by Eq. (16). The free chloride in mg/litre is given by Eq. (43) multiplied by 10^3 mmole/mole. The total chloride content is:

$$c_{bound} = a \cdot \left(0.02 \cdot K\right)^b \quad \text{mg/g cement gel} \tag{49}$$

or

$$c_{bound} = a \cdot (0.02 \cdot K)^{b} \cdot 10^{-3} \quad \text{kg/kg cement gel} \tag{49a}$$

Inserting Eq. (17) gives the total weight of bound chloride:

$$\left(Q_{Cl^{-}bound}\right)_{thr} = 1.25 \cdot \alpha \cdot C \cdot a \cdot (0.02 \cdot K)^{b} \cdot 10^{-3} \quad \text{kg} \tag{50}$$

Dividing by C and multiplying by 100 gives the bound chloride in weight-% of cement:

$$\left(Q_{Cl^{-}bound}\right)_{C,thr} = 0.125 \cdot \alpha \cdot a \cdot (0.02 \cdot K)^{b} \quad \text{weight-\% of cement.} \tag{50b}$$

Thus, the bound chloride is directly proportional to the degree of hydration.

Total chloride

Alt 1 and Alt 3:

$$\left(Q_{Cl^{-}total}\right)_{C,thr} = 0.125 \cdot \alpha \cdot a \cdot (0.02 \cdot K)^{b} + 0.71 \cdot K \cdot 10^{-1} \cdot (w_0 / c - 0.39 \cdot \alpha) \quad \text{weight-\%} \tag{51}$$

Alt 2:

$$\left(Q_{Cl^{-}total}\right)_{C,thr} = 0.125 \cdot \alpha \cdot a \cdot (0.02 \cdot K)^{b} + 0.71 \cdot K \cdot 10^{-1} \cdot (w_0 / c - 0.19 \cdot \alpha) \quad \text{weight-\%} \tag{52}$$

13.3 Calculated threshold chloride contents in weight-% of cement – total leaching

Chloride binding is supposed to be described by Figure 6; i.e. the coefficients a and b are a=13.5, b=0.41. Hausmann criterion is supposed to be valid; i.e. K=0.6.

Then the threshold values in Table 19 are valid.

Table 19: Threshold concentration of free, bound and total chloride in weight-% of cement.

w_o/c	α	Threshold chloride concentration (weight-% of cement)					
		Alt 1; Alt 3			Alt 2		
		free	bound	total	free	bound	total
0.60	0.75	0.013	0.206	**0.22**	0.019	0.206	**0.23**
0.50	0.70	0.009	0.193	**0.20**	0.016	0.193	**0.21**
0.40	0.65	0.006	0.179	**0.19**	0.012	0.179	**0.19**
0.30	0.50	0.004	0.138	**0.14**	0.009	0.138	**0.15**

The threshold concentration is very low when concrete is totally leached out of alkali.

The effect of partial leaching is calculated by exchanging the parameter 0.71 in Eq. (47), (48), (51), (52) for the parameter $35.5 \cdot [OH^{-}]$. The parameter 0.02 in Eq. (50), (51) and (52) is exchanged for the parameter $[OH^{-}]$.

Example:
The pH-value in a concrete with w/c-ratio 0.40 and 65% hydration is found to be 13.2; i.e. $\left[OH^-\right] = 10^{13.2-14} = 0.158$ mole/litre after partial leaching.

The parameter, $35.5\cdot\left[OH^-\right] = 35.5\cdot 0.158 = 5.61$.

Inserting the exchanged values in Eq. (51) gives the following threshold concentration of total chloride. (Alt 3 is supposed to be valid):

$$\left(Q_{Cl^- total}\right)_{C,thr} = 0.125\cdot 0.65\cdot 13.5\cdot \left(0.158\cdot 0.6\right)^{0.41} + 5.61\cdot 0.6\cdot 10^{-1}\cdot\left(0.40-0.39\cdot 0.65\right)$$

or

$$\left(Q_{Cl^- total}\right)_{C,thr} = 0.417 + 0.049 = 0.47 \quad \text{weight-\% of cement}$$

The threshold concentration is increased by 250% in comparison to the completely leached concrete. It is however considerably lower than for the un-leached concrete, c.f. Table 6 for a high alkali cement and Table 7 for a low alkali cement.

14. EFFECT OF MOISTURE LEVEL ON THE THRESHOLD CHLORIDE CONTENT

14.1 Effect of RH on the alkalinity of pore water and on the threshold concentration of free chloride

The analysis above is based on completely water saturated concrete (except for air-pores and pores in aggregate). The fact that concrete is not always saturated has been verified by analysis of the moisture content stored for long time in water or sea water. The phenomenon is particularly marked in concrete with low w/c-ratio like *High Performance Concrete*. The reason might be that continued hydration gives a self-desiccating effect occurring more rapidly than water can enter the dense pore structure.

When the concrete is non-saturated (RH<100%) the amount of pore solution is lower than in saturated concrete. The content of alkali is however unchanged. Therefore, the concentration of OH^--ions will be higher. The amount of pore water is given by the sorption isotherm for water. Desorption isotherms are seen in Figure 7; Nilsson (1977). Hysteresis between desorption and adsorption of water is neglected. Therefore the isotherms in Figure 7 are supposed to be valid also at adsorption.

Total water content, w_e (kg/m^3) related to the cement content at different RH is shown in Table 20. Corrosion will hardly take place at RH<70%. Therefore, water contents below that are not shown. The maximum corrosion rate often occurs around the RH-region 95%

Table 20: Water content in Portland cement concrete as function of RH. The figures are taken from Figure 7.

w_o/c	α	RH (%)				
		Water content, w_e/c (litre/kg cement)				
		70	80	90	95	100$^{1)}$
0.6	0.8	0.215	0.260	0.335	0.370	0.450
0.5	0.8	0.195	0.235	0.275	0.305	0.350
0.4	0.6	0.170	0.195	0.225	0.250	0.290
0.3	0.5	0.135	0.150	0.170	0.180	0.205

1) Equal to the entire pore volume divided by cement, w_{tot}/c, see Eq. (5)

The alkalinity of pore water depends on which part of the pore water dissolves alkali. The three alternatives are illustrated by Fig 1. Only Alt 3 is considered below.

The total water content W is:

$$W_e = (w_e / c) \cdot C = w_e \quad \text{litre} \tag{53}$$

Where the parameter w_e/c is the value found in Table 19. C is the amount of cement. The OH^- -concentration is:

$$\left[OH^-\right] = \frac{k \cdot C}{W_e} = \frac{k \cdot C}{w_e / c \cdot C} = \frac{k}{w_e / c} \quad \text{mole/litre} \tag{54}$$

where k is the water soluble alkali expressed as mole OH^-/kg cement.

The threshold concentration of free chloride is:

$$\left[Cl^-{}_{free}\right]_{thr} = K \cdot \frac{k}{w_e / c} \quad \text{mole/litre} \tag{55}$$

or

$$\left(Cl^-{}_{free}\right)_{thr} = 35.5 \cdot K \cdot \frac{k}{w_e / c} \quad \text{g/litre} \tag{56}$$

In Table 21 calculated values of the threshold value of free chloride are given. It is assumed that high alkali cement is used with Na_2O content 1.29 weight-% (i.e. k=0.416) and that K=0.6 (the Housmann criterion).

Table 21: Effect of RH on the threshold value of free chloride. Degree of hydration as in Table 19. k=0.416, K=0.6. Alkali and chloride distribution according to Alt 3.

w_o/c	$\left(Cl^-{}_{free}\right)_{thr}$ (g/litre)				
	RH (%)				
	70	80	90	95	100
0.6	**41**	**34**	**27**	**24**	**20**
0.5	**45**	**38**	**32**	**29**	**25**
0.4	**52**	**46**	**39**	**35**	**31**
0.3	**66**	**59**	**52**	**49**	**43**

Drying causes considerable increase in the threshold concentration. For w/c-ratio 0.4 the increase in threshold concentration is 25% when concrete is dried to equilibrium with 90% RH. For w/c-ratio 0.60 the increase is 35%.

14.2 Effect of RH on the threshold value in weight-% of cement

Only Alt 3 is considered below, i.e. only capillary pores are assumed to dissolve chloride but all water is assumed to dissolve alkali.

Free chloride

The pore volume containing water able to dissolve chloride is:

$$V_{P,Cl^-} = \left(w_e/c\right)\cdot C - 0.20\cdot\alpha\cdot C = C\cdot\left(w_e/c - 0.20\cdot\alpha\right) \text{ litres} \qquad (57)$$

where the parameter 0.20·α·C is the volume of gel pores in litres/m^3 which is not able to dissolve chloride.

The total amount of free chloride in 1 m^3 of concrete at threshold concentration is:

$$\left(Q_{Cl^-\,free}\right)_{thr} = \left(Cl^-{}_{free}\right)_{thr}\cdot 10^{-3}\cdot C\cdot\left(w_e/c - 0.20\cdot\alpha\right) \quad \text{kg} \qquad (57)$$

Inserting Eq. (55) gives:

$$\left(Q_{Cl^-\,free}\right)_{thr} = 35.5\cdot K\cdot\frac{k}{w_e/c}\cdot 10^{-3}\cdot C\cdot\left(w_e/c - 0.20\cdot\alpha\right) \quad \text{kg} \qquad (57b)$$

Dividing by C and multiplying by 100 gives the threshold free chloride in weight-% of cement:

$$\left(Q_{Cl^-\,free}\right)_{C,thr} = 3.55\cdot K\cdot\frac{k}{w_e/c}\cdot\left(w_e/c - 0.20\cdot\alpha\right) \quad \text{weight-\% of cement} \qquad (58)$$

where w_e/c is obtained from Table 20.

Calculated values of the threshold *free* chloride in weight-% of cement for different RH are shown in Table 22. The calculation is based on the Hausmann criterion (K=0.6), high alkali cement (k=0.416), and sorption isotherm shown in Figure 6 (a=13.5, b=0.41).

Table 22: Influence of RH in concrete on the threshold free chloride concentration. Moisture contents in Table 19 are used. Alkali and chloride distribution according to Alt 3.

w_o/c	α	$\left(Q_{Cl^- total}\right)_{C,thr}$ (weight-%) Alt 3				
		RH (%)				
		70	80	90	95	100
0.6	0.8	**0.23**	**0.34**	**0.46**	**0.51**	**0.57**
0.5	0.8	**0.16**	**0.28**	**0.37**	**0.43**	**0.48**
0.4	0.6	**0.26**	**0.34**	**0.42**	**0.46**	**0.52**
0.3	0.5	**0.23**	**0.37**	**0.36**	**0.40**	**0.46**

The threshold free amount of chloride in weight-% of cement decreases with decreased RH despite the fact that the threshold free chloride concentration increases, see Table 20. The reason is that, according to Alt 3, the volume of pore water able to dissolve chloride decreases even more rapidly with reduced RH; see Figure 57

> *Example, w/c=0.40:*
> Threshold free concentration is 40% higher at RH 70% than at RH 100% (Table 20)
> Pore volume able to dissolve chloride is 70% lower at RH 70% than at RH 100% (Eq. 57)

Bound chloride

The amount of bound chloride in weight-% of cement is obtained by Eq. (18). In this equation bound chloride is expressed by the parameter c_{bound} which is the amount of bound chloride in mg/g cement gel, or 10^{-3} kg/kg.

c_{bound} is obtained from the binding isotherm; see Fig. 6. This can be expressed by Eq. (16). The concentration of free chloride c_{free} included in this equation is defined by Eq. (19). Inserting Eq. (55) in this gives for the threshold concentration of free chloride:

$$\left(c_{free}\right)_{thr} = K \cdot \frac{k}{w_e / c} \quad \text{mole/litre} \tag{59}$$

c_{bound} at threshold concentration becomes:

$$\left(c_{bound}\right)_{thr} = a \cdot \left(K \cdot \frac{k}{w_e / c} \right)^b \quad \text{mg/g gel} \tag{60}$$

The bound chloride as weight-% of cement is described by Eq. (18):

$$\left(Q_{Cl^- bound}\right)_{C,thr} = 0.125 \cdot \alpha \cdot a \cdot \left(K \cdot \frac{k}{w_e / c} \right)^b \quad \text{weight-\% of cement} \tag{61}$$

Calculated values of the threshold *bound* chloride in weight-% of cement for different RH are shown in Table 23. The calculation is based on the Hausmann criterion (K=0.6), high alkali cement (k=0.416), and sorption isotherm shown in Figure 6 (a=13.5, b=0,.41).

Table 23: Influence of RH in concrete on the threshold bound chloride concentration. Moisture contents in Table 20 are used. Alkali and chloride distribution, Alt 3.

w_o/c	α	$\left(Q_{Cl^- total}\right)_{C,thr}$ (weight-%)				
		RH (%)				
		70	80	90	95	100
0.6	0.8	**1.44**	**1.33**	**1.20**	**1.15**	**1.06**
0.5	0.8	**1.50**	**1.39**	**1.30**	**1.25**	**1.18**
0.4	0.6	**1.19**	**1.12**	**1.06**	**1.01**	**0.95**
0.3	0.5	**1.08**	**1.04**	**0.99**	**0.97**	**0.92**

The threshold value of total chloride increases with decreased RH which depends on the higher alkalinity of pore water. The effect is predicted by the binding isotherm; see Figure 6.

The fact that the amount of bound chloride is decreased with decreased w/c-ratio is explained by the lower degree of hydration.

Total chloride

The total threshold chloride content in weight-% of the cement is:

$$\left(Q_{Cl^- total}\right)_{C,thr} = 0.125 \cdot \alpha \cdot a \cdot \left(K \cdot \frac{k}{w_e / c} \right)^b + 3.55 \cdot K \cdot \frac{k}{w_e / c} \cdot \left(w_e / c - 0.20 \cdot \alpha \right) \quad \text{weight-\%} \quad (62)$$

Calculated values of the threshold *total* chloride in weight-% of cement for different RH are shown in Table 24. The calculation is ased on the Hausmann criterion (K=0.6), high alkali cement (k=0.416), and sorption isotherm shown in Figure 6 (a=13.5, b=0,.41).

Table 24: Influence of RH in concrete on the threshold total chloride concentration. Moisture contents in Table 20 are used. Alkali and chloride distribution according to Alt 3.

w_o/c	α	$\left(Q_{Cl^- total}\right)_{C,thr}$ (weight-%) Alt 3				
		RH (%)				
		70	80	90	95	100
0.6	0.8	1.67	1.67	1.66	1.66	1.63
0.5	0.8	1.66	1.67	1.67	1.68	1.66
0.4	0.6	1.45	1.46	1.48	1.47	1.47
0.3	0.5	1.31	1.41	1.35	1.37	1.39

The values are remarkably independent on the moisture content. This depends on the fact that the threshold free chloride decreases with decreased RH whereas the threshold of bound chloride increases by about the same relative amount..

> *Note:*
> The values for RH 100% differs by a small amount from the values in Table 6. The reason is that the assumed degrees of hydration are not exactly the same, except for w/c=0.50 for which the agreement is good.

An *empirical* expression for the relation between the threshold value of total chloride and degree of hydration of concrete made with the actual high alkali Portland cement and based on the data in Table 23 and valid for all RH and all w/c-ratios is:

$$\left(Q_{Cl^- total}\right)_{C,thr} = 0.88 + \alpha$$

Also the data from Table 6 at RH 100% satisfy this equation almost perfectly.

The equation indicates that in fact no hydration is needed for a certain threshold value to appear. This limiting value is 0.88 weight-%. This value is also predicted by the theoretical Eq. (62). When the degree of hydration is zero, the water content w_e/c is equal to the w/c-ratio w_o/c. Then, Eq. (62) is written:

$$\left(Q_{Cl^- total}\right)_{C,thr} = 3.55 \cdot K \cdot k \quad \text{weight-\%} \qquad (62a)$$

Inserting values for K and k gives:

$$\left(Q_{Cl^{-}total}\right)_{C,thr} = 3.55 \cdot 0.6 \cdot 0.416 = 0.88 \quad \text{weight-\%}$$

14.3 Effect of alkalinity of cement on the chloride threshold in weight-%

The free chloride threshold is directly proportional the alkalinity of cement, k; Eq. (58).

The bound chloride threshold is proportional to the parameter $(k)^b$, Eq. (61) provided the coefficient K and the water content is unchanged.

The threshold value of total chloride for a cement with other alkalinity than the cement treated above (k=0.41) can therefore be calculated from the values in Table 23 using these proportionalities. For a low alkali cement with alkalinity 0.5% (k=0.161) the values in Table 25 are valid.

Table 25: Influence of RH in concrete on the threshold total chloride concentration. Low alkali cement (k=0.161). Alkali and chloride distribution according to Alt 3.

w_o/c	α	$\left(Q_{Cl^{-}total}\right)_{C,thr}$ (weight-%) Alt 3				
		RH (%)				
		70	80	90	95	100
0.6	0.8	**1.07**	**1.03**	**0.99**	**0.98**	**0.94**
0.5	0.8	**1.08**	**1.05**	**1.02**	**1.02**	**0.99**
0.4	0.6	**0.91**	**0.89**	**0.88**	**0.86**	**0.84**
0.3	0.5	**0.82**	**0.84**	**0.81**	**0.82**	**0.80**

The threshold value before any hydration is changed to 0.88·(0.161/0.416)=0.34 weight-%.

15. EFFECT OF CARBONATION ON THE THRESHOLD CHLORIDE CONTENT

When concrete carbonates alkali hydroxides and calcium hydroxide (portlandite) are transformed to carbonates. The pH-value of the saturated pore solution will not be higher than 9. Therefore, the OH^--concentration is not higher than:

$$\left[OH^-\right] < 10^{9-14} = 10^{-5} \quad \text{mole /litre} \tag{63}$$

The threshold chloride concentration is:

$$\left[Cl^-\right]_{thr} < K \cdot 10^{-5} \quad \text{mole/litre} \tag{64}$$

The consequence of this very low threshold concentration is that corrosion will be initiated in a bar enclosed by carbonated concrete, as soon as any chloride reaches the bar i.e.:

$$\left(Q_{Cl^{-}total}\right)_{C,thr} \approx 0 \quad \text{weight-\% of concrete} \tag{65}$$

A negative side-effect of carbonation is that chloride that had been bound in un-carbonated concrete is released when this is carbonated. Thus, if the free chloride was fairly low before carbonation it might become high as a result of carbonation.

16. EFFECT OF THICKNESS OF COVER ON THE THRESHOLD CHLORIDE CONTENT

According to the basic assumption on which this report is based, corrosion starts when the chloride concentration transgresses a threshold value given by Eq. (2). According to Hausmann the coefficient K in the equation is 0.6. This value is based on tests of steel in bulk chloride solutions. It is assumed above that the same value might be used also for steel embedded in concrete. However, there is a possibility that the coefficient depends on the thickness of the concrete cover. Factors of importance for corrosion such as oxygen concentration and stability of moisture condition are probably more favourable at greater depth from the concrete surface.

It might even be that the value K can become so high that corrosion cannot be initiated at normal chloride environments of interest for concrete construction, i.e. normal exposure to de-icing salt and sea water. The idea is illustrated by Figure 9. For a certain concrete the cover is X mm. This corresponds to $K=K_X$. The threshold chloride concentration for K_X is $K_X \cdot [OH^-]$. This value is higher than the actual chloride concentration in the concrete. Therefore corrosion is impossible. Corrosion can only be initiated when the cover is smaller than Y.

The idea put forward above is only a hypothesis. The effect of cover thickness on the threshold chloride concentration has not been thoroughly investigated.

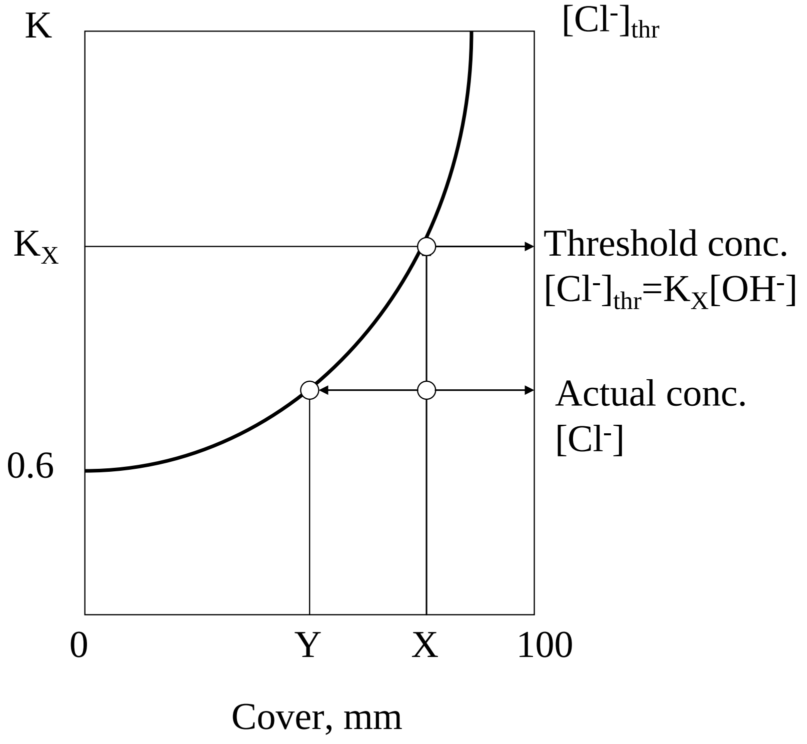

Figure 9: The effect of concrete cover on the threshold concentration of free chloride. Hypothesis.

17. EFFECT OF DEFECT BOND BETWEEN STEEL AND CONCRETE ON THE THRESHOLD CHLORIDE CONTENT

When the reinforcement bar is not completely enclosed by concrete – see Figure 10- the chloride threshold value will normally be reduced. Two cases are imaginable:

Case 1: The defect, i.e. the space between the steel surface and surrounding cement paste, is constantly water-filled.
Case 2: The defect cannot become water-filled, or it is just water-filled during short periods.

Case 1 principally corresponds to a defect-free concrete, since water in contact with the steel surface will have almost the same alkalinity as the rest of the pore water. Therefore, the threshold value might be almost unchanged.

In Case 2 the steel surface does not stay in contact with alkaline water. Therefore, principally the threshold value ought to be close to zero. However, both OH^--ions and Cl -ions will migrate along the steel surface within the adsorbed or condensed water layer which always is present on the surface. Exactly which concentration of these ions that will be reached at the surface is not known. Probably, however, it is lower than the values valid for perfectly cast-in steel. Therefore, the threshold chloride value is reduced.

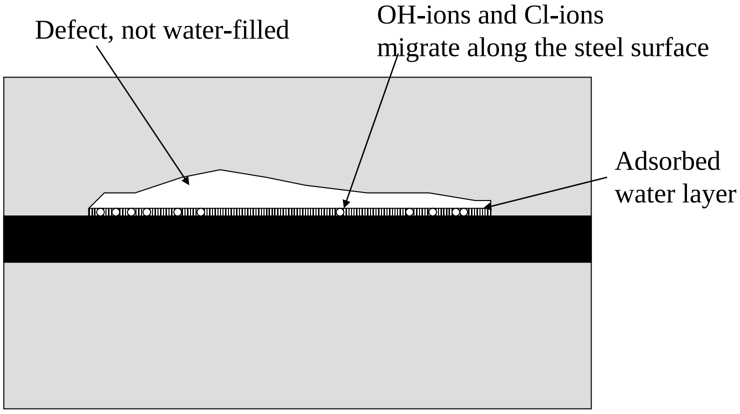

Figure 10: Reinforcement bar with defect bond. Despite the fact that the defect is "dry" OH-ions might migrate within the adsorbed water layer thereby cause a certain increase in the threshold chloride level.

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APPENDIX 1[3]

The determination described below is based on analyses of specimens that are immersed in one or more baths containing chloride ions of known concentration.

METHOD FOR 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 6) that a unit weight of the “cement gel” (hydration product) always binds the same amount of chloride at a given free chloride concentration. 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):

$$Q_{bound} = c_{b,gel} \cdot Q_{gel}' = c_{b,gel} \cdot 1.25 \cdot \alpha \cdot C' \cdot V \qquad (A1)$$

Where Qgel´ is the amount of cement gel in the specimen (g). 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:

$$w_w = C' \cdot (w/c - \gamma \cdot \alpha) \cdot V \qquad (A2)$$

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:

$$Q_{free} = c''' \cdot w_w = c''' \cdot C' \cdot (W/C - \gamma \cdot \alpha) \cdot V \qquad (A3)$$

where c´´´ is the chloride concentration in the bath in which specimens are immersed (the same as in the pore water) (g/cm^3)

The total chloride content is determined experimentally. It becomes:

$$Q_{tot} = Q_{bound} + Q_{free} = c_{b,gel} \cdot 1.25 \cdot \alpha \cdot C' \cdot V + c''' \cdot C' \cdot (W/C - \gamma \cdot \alpha) \cdot V \qquad (A4)$$

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

$$\boxed{c_{b,gel} = [Q_{tot} - c''' \cdot C' \cdot (W/C - \gamma \cdot \alpha) \cdot V / [1.25 \cdot \alpha \cdot C' \cdot V] \qquad (A5)}$$

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.

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[3] Extract from the report: Fagerlund, G. Imaginable effects of limestone filler on chloride transport. Div. Building Materials. Lund Institute of Technology. Report TVBM-7187, 2005.

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 A1.

> Note: Equation (A1), and equation (A2) 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.

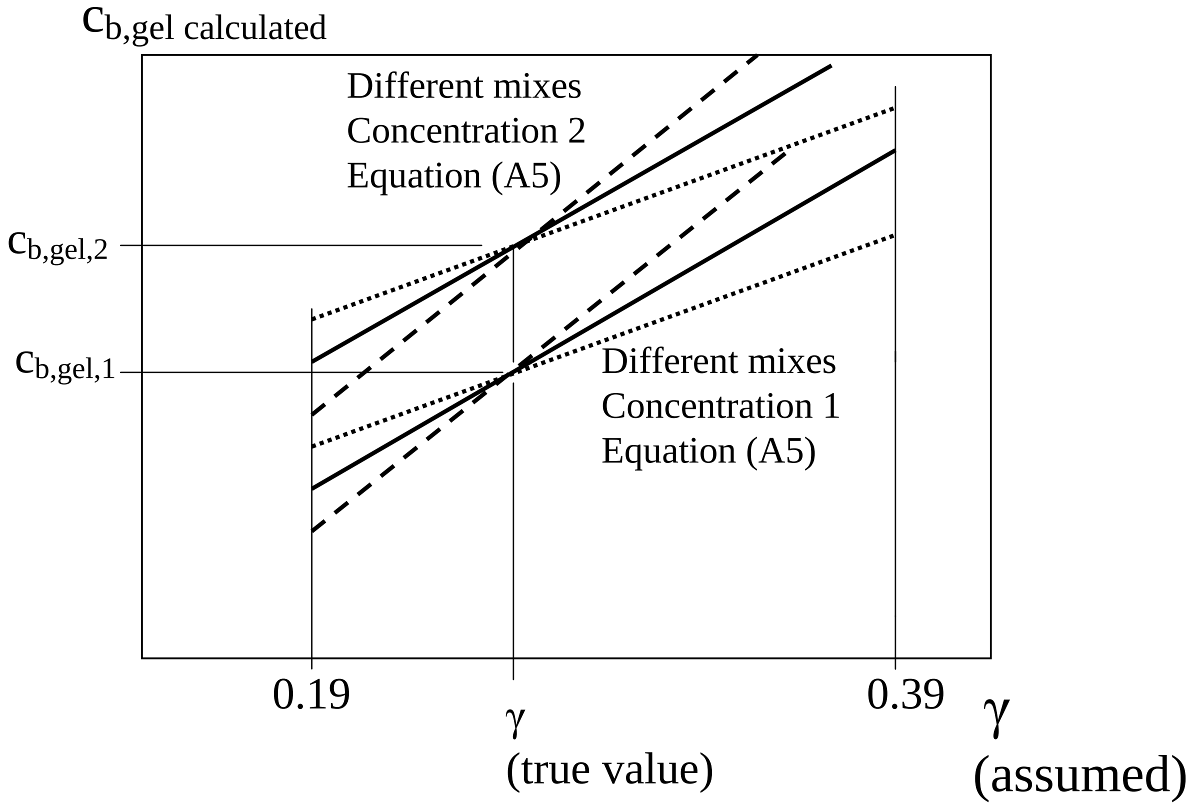

Figure A1: Determination of the coefficient γ in equation (A5).

APPENDIX 2

EFFECT OF LEACHING ON THE THRESHOLD CHLORIDE CONTENT

OH-ions will gradually be leached out of concrete when this is submerged in water. An example of leaching from a concrete with w/c-ratio 0.55 after 36 years in the North Sea is shown in Figure A2.1 [4]. On the depth 30 mm from the surface the pH-value for all locations of the structure is 12.6 almost exactly corresponding to the saturation concentration of calcium hydroxide. This means that all more soluble alkalis, NaOH and KOH, have been leached out completely on this depth.

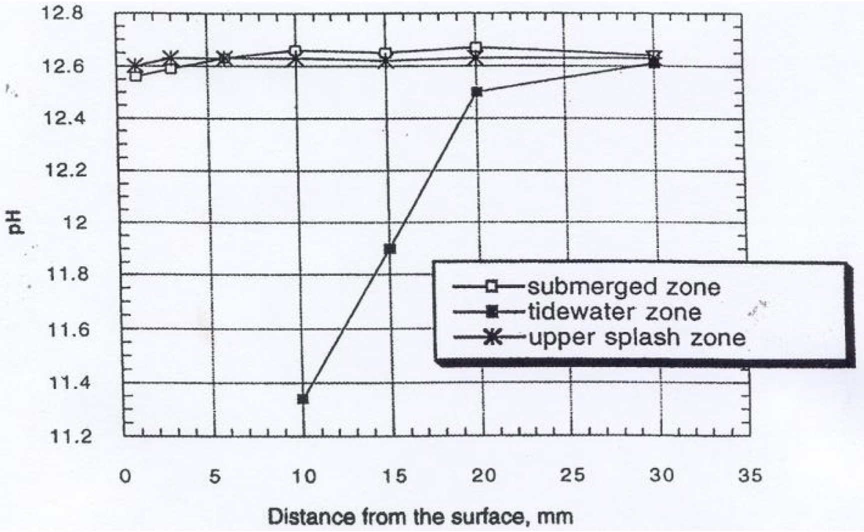

Figure 4.1: pH-profile in the surface part of a concrete structure exposed for 36 years to water in the North Sea.

Leaching can be calculated by Fick´s 2:nd law. In the case where a substance is leaving the material, and the outer OH-concentration is zero (pH7), the solution of the equation is:

$$\frac{[OH]_{x,t}}{[OH]_0} = erf\left[\frac{x}{(4\cdot\delta_{OH}\cdot t)^{1/2}}\right] \tag{A2.1}$$

Where $[OH]_{x,t}$ is the OH-concentration on distance x from the surface at time t, and $[OH]_0$ is the initial OH-concentration before leaching. δ_{OH} is the diffusion coefficient of OH-ions. Most interesting is the OH-concentration at the surface of the reinforcement bar. Therefore, in the equation x shall be replaced by the cover T.

The equation can be used for a parameter study of the effect of diffusivity and cover on the OH-concentration at the reinforcement bar. An example of a calculation of leaching is made below. The cement is of type low alkali with $Na_2O_{equivalent}$ 0.5 weight-%. Then, the coefficient

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[4]) Sandberg, P.: Unpublished results from the Swedish Cooperative Project “Marine Concrete Structures”. Div. Building Materials, Lund Institute of Technology, Lund 1993. (Similar results from field exposure are presented in Sandberg, P.: Chloride initiated reinforcement corrosion in marine concrete. Div. Building Materials, Lund Institute of Technology, Report TVBM-1015, Lund 1998).

k is 0.161 mole OH^- per kg cement; see paragraph 5.2. The water-cement ratio is 0.40 and the degree of hydration 65%. The initial concentration is in all cases given by Eq. (7) (OH from $CaOH_2$ is neglected):

$$\left[OH^-\right] = \frac{0.161}{0.4 - 0.19 \cdot 0.65} = 0.58 \quad \text{mole/litre}$$

Solution of Eq. (A2.1) for different chloride transport coefficients (10^{-12} and $5 \cdot 10^{-12}$ m^2/s) and different exposure times (10 and 50 years) is shown in Figure A2.1.

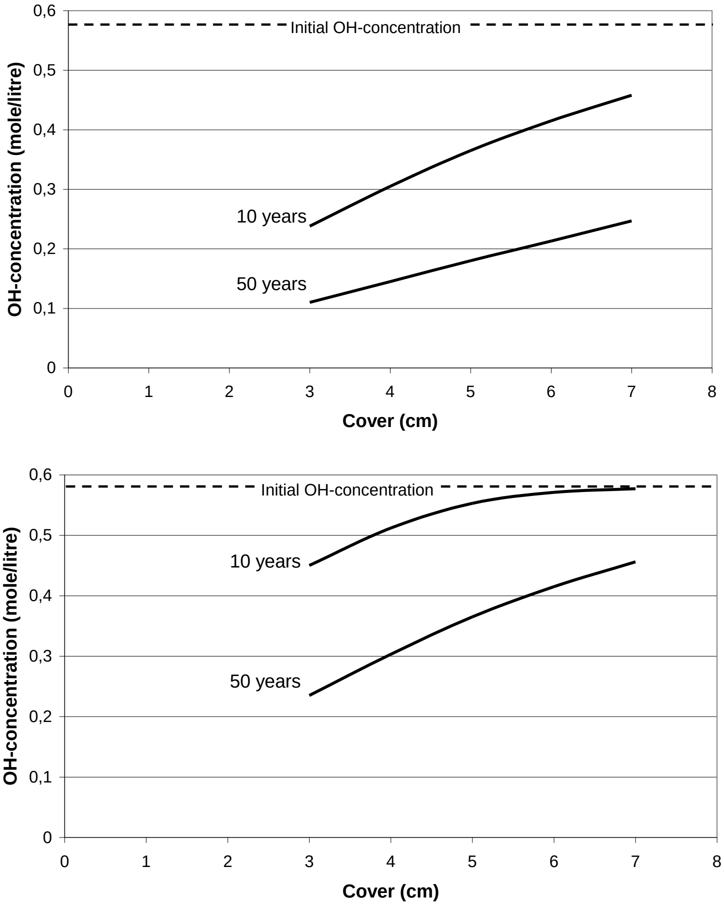

Figure A2.1: OH-concentration as function of the depth from the surface. Upper: Transport coefficient $5 \cdot 10^{-12}$ m^2/s. Lower: Transport coefficient 10^{-12} m^2/s.

Example:
Cover 50 mm. Transport coefficient is $5 \cdot 10^{-12}$ m^2/s. Exposure time 50 years.

The OH-concentration is 0.18 mole/litre; see the upper figure. pH=13.25.

The threshold content of *free chloride* in weight-% of the cement is calculated by Eq. (37). The coefficient K=0.6. Ion distribution Alt 3.:

$$\left(Q_{Cl^- free}\right)_{C.thr} = 3.55 \cdot 0.6 \cdot 0.18 \cdot (0.4 - 0.19 \cdot 0.65) = 0.106 \quad \text{weight-\%.}$$

The threshold content of *bound chloride* is calculated by Eq. (28b). The coefficient k in the equation is calculated by Eq. (7):

$$k = 0.18 \cdot (0.4 - 0.19 \cdot 0.65) = 0.05 \quad \text{mole OH}^- \text{ per kg cement.}$$

$$\left(Q_{Cl^- bound}\right)_{C,thr} = 0.125 \cdot 0.65 \cdot 13.5 \cdot \left(\frac{0.6 \cdot 0.05}{0.4 - 0.19 \cdot 0.65}\right)^{0.41} = 0.441 \quad \text{weight-\%}$$

The threshold content of *total chloride* is:

$$\left(Q_{Cl^- total}\right)_{C,thr} = 0.106 + 0.441 = 0.55 \quad \text{weight-\%}$$

For the un-leached concrete with the same cement type, the threshold total chloride is 0.89 weight-%, i.e. about 60% higher value; see Table 7.

Conclusion

For long leaching time and thin cover, leaching causes a substantial reduction of the threshold concentration.