CHLORIDE THRESHOLD VALUES FOR SERVICE LIFE DESIGN

(This paper is a reprint of an identical paper first presented at the RILEM Workshop TMC in Paris, September 2000)

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ABSTRACT

An estimation of the chloride ingress into concrete has little value for practice until the threshold value in the particular situation is known. When chloride penetrates the concrete cover and reaches the steel reinforcement a corrosion process will initiate when a certain chloride concentration (*the threshold value*) is reached.

It is known from the literature that not only the type of concrete but also the exposure conditions (local environments) are decisive for the magnitude of the threshold value. Therefore results from natural exposure and laboratory exposure must be compiled together in order to estimate threshold values for the engineering service life design.

A new approach for laboratory experiments is being developed so that chloride threshold levels in laboratory tests can be measured as chloride concentrations in the bulk concrete.

The paper presents an engineering approach were threshold values for ordinary concrete with silica fume and/or fly ash can be calculated from a formula based on data from the literature. When new types of concrete shall be evaluated the presented laboratory test method can be used.

1. INTRODUCTION

The determination of chloride threshold values, i.e. the chloride concentration at which mild steel reinforcement will start corroding in concrete is the subject for a number of research projects. This paper reintroduces recent findings given in the HETEK project, cf. Frederiksen et al [1997] and presents a new attempt for reliable determination of chloride threshold values in laboratory experiments.

In Frederiksen et al. [1997], *P. Sandberg* estimated chloride threshold values for different binders and for different environments including those mentioned above. The estimates were made on the basis of experimental data reported in the literature. That review is reintroduced below and supplemented with more considerations for the road environment.

Unfortunately no simple way exists for the translation of short-term corrosion data from the laboratory, or even short-term data from field exposure, into values that can describe the long-term behaviour of a field exposed structure.

Chloride threshold levels and active corrosion rates depend strongly on the cover thickness, for a given concrete quality exposed to a given set of exposure conditions. Therefore it is not possible to obtain quantitative corrosion data from direct measurements on high performance concrete with thick covers, because of the very long initiation period required.

2. EVALUATION OF PUBLISHED CHLORIDE THRESHOLD LEVELS

Modern concrete structures exposed to a severe environment typically have a low water to binder ratio (often less than *w/b* = 0.40) and a thick specified cover (often more than 45 mm). These measures do not only increase the penetration time for the chloride to reach the steel surface, they also minimise moisture and temperature variations at the depth of the reinforcement, thereby increasing the chloride threshold.

Unfortunately field exposure tests with such thick covers would be extremely time consuming before any chloride thresholds could be evaluated. As a consequence, chloride thresholds have been estimated in basically four different ways of testing, none of them being capable alone to simulate the field conditions in a modern structure:

A) Field testing of modern low *w/b* ratio laboratory cast concrete specimen, with small covers (normally in the range 10-20 mm) - *missing the effects of cover and of variable compaction in practise.*

B) Laboratory testing of modern low *w/b* ratio concrete, sometimes with the environmental impact simulated by potentiostatically controlled steel potentials - *missing the effects of cover and of variable compaction, and usually also the effect of a varying microclimate and of leaching of alkali hydroxide.*

C) Field studies of existing good quality old structures, with covers > 30 mm but with higher *w/b* ratios (typically > 0.5) - *missing the effect of a low w/b ratio and the effect of new binders.*

D) Laboratory or field testing of concrete with cast-in chloride, thereby allowing for the use of low *w/b* ratio concrete and a thick cover - *missing the effect of steel passivation in chloride free concrete.*

Procedure D) is considered to be the most erroneous one, since the presence of cast in chloride decrease the ability of the cement paste to passivate the steel. Furthermore, the concrete porosity and the composition of some of the cement hydrates are altered if cast-in chloride is present during most of the curing.

Results from procedure A) - C) will all give some erroneous conclusions if not evaluated with care. No procedure yet exists which has proven to be scientifically correct for the evaluation of long term threshold levels. Therefore, an engineering approach has been used as shown by the following examples:

Example 1

OPC Concrete with *w/b* = 0.50 exposed to a marine splash water, reported results on chloride threshold levels by weight of cement, according to procedure A-C):

A) 0.6-1.9 % Cl. Thomas [1995], Pettersson [1996].

B) 1.1-2.7 % Cl. Arup [1996], Breit [1994].

C) 0.3-1.4 % Cl. Henriksen [1993], Lukas [1985], Vassie [1984].

Chloride threshold levels < 0.4 % Cl reported from existing structures (procedure C) are generally associated with failure to comply with required cover, or associated with large compaction voids, a high w/c ratio, and similar major defects. On the other hand, threshold levels from “macro defect free” specimens exposed in the laboratory at constant exposure conditions seems to indicate far too optimistic threshold levels for a dynamic exposure zone such as the splash zone. The threshold levels obtained by field exposure of laboratory cast specimens seem to be the most suitable values for describing chloride threshold in high performance concrete which is cast and placed properly. Chloride thresholds according to procedure A should be on the safe side, since they do not take the stabilising effect of a thicker cover into account.

Example 2

OPC Concrete with *w/b* = 0.50 exposed in a marine submerged zone, reported results on chloride threshold levels by weight of cement, according to procedure A-C):

A) 1.5-2.0 % Cl$^-$ Pettersson [1996].

B) 1.6-2.5 % Cl– Arup [1996], Breit [1994].

C) > 2.0 % Cl$^-$ Sandberg [1995], Pettersson [1996].

The chloride threshold levels found in submerged concrete with procedure A-C seem to vary less as compared to the thresholds in the splash zone. This is probably because of the stable and relatively similar exposure conditions. The lower values according to procedure A are probably a result of smaller cover and of hydroxide leaching in the field exposure test. Therefore, these values should be on the safe side.

3. COMPILATION OF CHLORIDE THRESHOLD LEVELS

Some measured ranges of chloride threshold levels (black steel) in macro crack free concrete or mortar in various exposure regimes have been compiled and analysed in an excellent review by Glass and Buenfeld [1995], as shown in Table 1. Some additional chloride threshold levels have been reported as shown in Table 2.

Table 1. Measured ranges of chloride threshold levels (black steel) in macro crack free concrete in various exposure regimes, Glass & Buenfeld [1995].

Total chloride %Wt. cement	**Free Chloride Mole/l**	**[Cl]/[OH]**	**Exposure Type**	**Reference**
0.17 - 1.4			Field	Stratful et al. [1975]
0.2 - 1.5			Field	Vassie [1984]
0.25			Field	West & Hime [1985]
0.25 - 0.5			Laboratory	Elsener & Böhni [1986]
0.3 - 0.7			Field	Henriksen [1993]
0.4			Outdoors	Bamforth & Chapman-Andrews [1994]
0.4 - 1.6			Laboratory	
0.5 - 2			Laboratory	Hansson & Sørensen [1990]
0.5			Outdoors	Schiessl & Raupach [1990]
0.5 - 1.4			Laboratory	Thomas et al. [1990]
				Tuutti [1993]
0.6			Laboratory	
1.6 - 2.5		3 – 20	Laboratory	Locke & Siman [1980]
1.8 - 2.2			Field	Lambert et al. [1991]
	0.14 - 1.8	2.5 - 6	Laboratory	Lukas [1985]
		0.26 - 0.8	Laboratory	Pettersson [1993]
				Goni & Andrade [1990]
		0.3	Laboratory	
		0.6	Laboratory	Diamond [1986]
		1 – 40	Laboratory	Hausmann [1967]
				Yonezawa et al. [1988]

Table 2. Additional chloride threshold levels (black steel) in macro crack free concrete in various marine or laboratory exposure regimes, Pettersson [1996], Pettersson and Sandberg [1996], Sandberg [1995], Arup [1996], Thomas [1995] and by Breit [1994].

	Submerged zone C_{cr} - %Cl of cement		Splash zone C_{cr} - %Cl of cement		Atmospheric zone C_{cr} - %Cl of cement	
Concrete type	Range	Procedure	Range	Procedure	Range	Procedure
w/b = 0.50						
100 % CEM I	1.5-2.0	A	0.6-1.9	A		
100 % CEM I	1.6-2.5	B	1.2-2.7	B	1.5-2.2	B
100 % CEM I	>2.0	C	0.3-1.4	C		
5 % SF	1.0-1.9	A				
5 % SF	0.8-2.2	B				
20 % FA			0.3-0.8	C		
w/b = 0.40						
100 % CEM I	>2.0	A	0.9-2.2	A		
100 % CEM I	>2,2	B				
5 % SF	>1.5	A				
w/b = 0.30						
100% CEM I	>2.2	A	>1.5	A		
5% SF	>1.6	A	>1.0	A		
20 % FA	1.4	A	0.7	A		

3.1 The effect of the concrete moisture state

The effect of relative humidity on the chloride threshold level in laboratory exposed mortars is shown in Figure 1, as presented by Pettersson [1996].

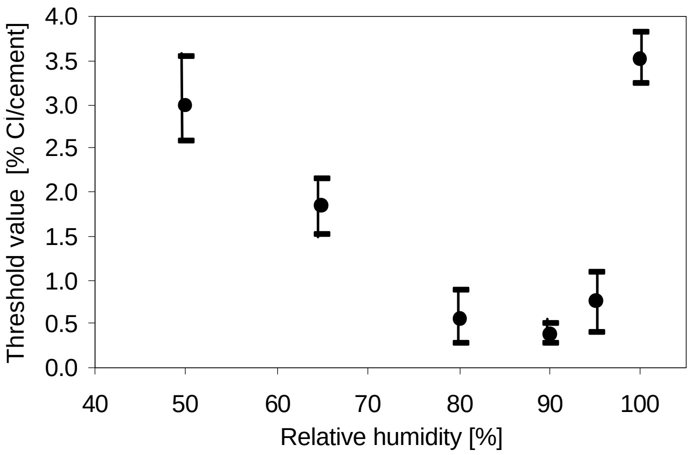


Figure 1. The effect of relative humidity on the chloride threshold level in laboratory exposed mortars, w/c ratio = 0.50, Pettersson [1996].

3.2 The effect of water to binder ratio

Pettersson and Sandberg [1996] as shown in Figure 2 illustrated the effect of water to binder ratio on the chloride threshold.

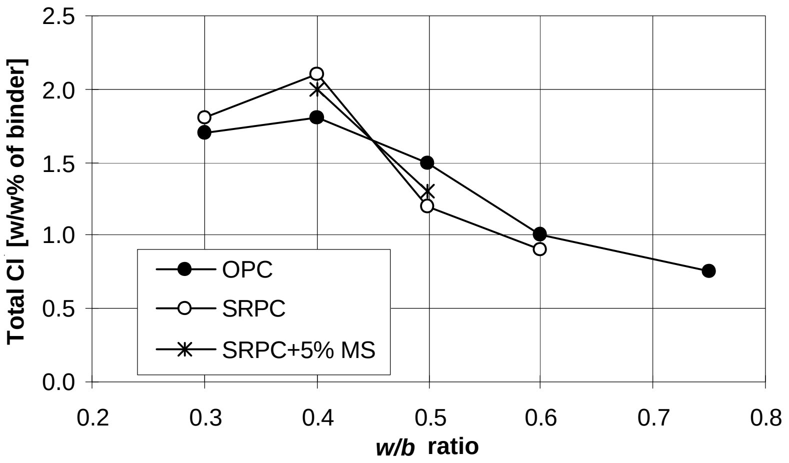


Figure 2. Chloride threshold levels measured on submerged concrete or mortar. Experimental results. Cover = 15 to 20 mm. Pettersson and Sandberg [1996].

3.3 The effect of mineral admixtures in concrete

Mineral admixtures have been found to decrease the chloride threshold level, as illustrated by Thomas [1996] for fly ash exposed in a marine splash zone, Figure 3. Pettersson [1993], [1996] has reported similar results for the effect of fly ash and silica fume.

Note that several investigations have indicated a very positive and decreasing effect of mineral admixtures on the corrosion rate. These findings are in most cases not related to direct studies of the chloride threshold, rather obtained from studies of the corrosion behaviour in the active state. The positive effect of mineral admixtures on the corrosion rate is attributed to the increase in concrete resistivity.

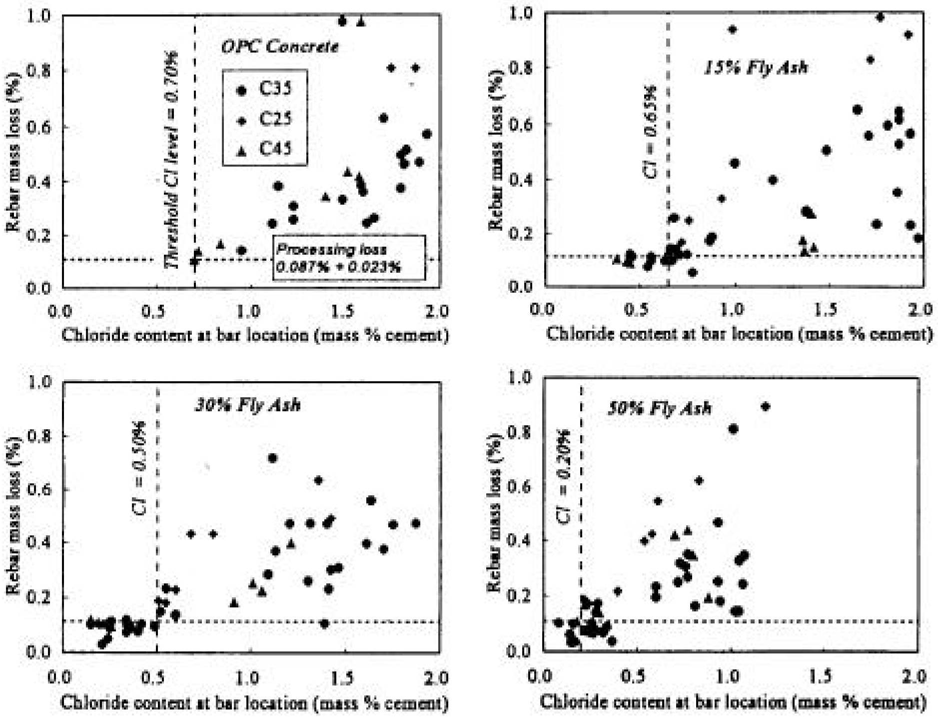


Figure 3. Chloride threshold levels and corrosion rates for OPC and fly ash concrete exposed in a marine splash zone in Canada, Thomas [1996].

The negative effect of mineral admixtures on the chloride threshold level is attributed to the decrease in alkalinity of the concrete pore solution, and to the decrease in calcium hydroxide at the steel-concrete interface, Sandberg [1995].

4. THE DEVELOPMENT OF CHLORIDE THRESHOLD LEVELS FOR DESIGN PURPOSES

The chloride threshold levels presented in Table 2 and Figures 1 and 3 indicate that the chloride threshold levels tend to decrease with the incorporation of mineral admixtures, and with an increasing *w/c* ratio. This behaviour is attributed to the decrease in the pH of the concrete pore solution caused by the incorporation of mineral admixtures, and by the diluting effect of an increasing *w/c* ratio, Sandberg [1995] and Pettersson [1996].

The threshold levels given in Table 1 are unfortunately presented in several different ways and sometimes lacking relevant information, which makes it very difficult to evaluate the results in a statistically correct way for design purpose. Therefore, a conservative engineering approach has been used as illustrated in the previous examples 1 and 2, to establish chloride threshold levels for design purpose as shown in Table 3. The relative differences in threshold levels between OPC and FA-concrete, between OPC and SF-concrete, and between OPC concrete of various *w/c* ratio, as found by Thomas [1996] and Pettersson [1996] respectively, has been maintained in the development of Table 3.

Table 3. Suggested design values for chloride threshold levels (black steel) in various Nordic exposure zones.*

Concrete type	submerged zone C_{cr} %Cl of PO (cement + puzzolanas)	marine splash zone C_{cr} %Cl of PO	de-icing salt splash zone C_{cr} %Cl of PO	atmospheric zone marine/de-icing C_{cr} %Cl of PO
w/b 0.50				
100 % CEM I	*1.5 %*	*0.6 %*	*0.4 %*	*0.6 %*
5 % SF	*1.0 %*	*0.4 %*	*0.3 %*	*0.4 %*
10 % SF	*0.6 %*	*0.2 %*	*0.2 %*	*0.2 %*
20 % FA	*0.7 %*	*0.3 %*	*0.2 %*	*0.3%*
w/b 0.40				
100 % CEM I	*2.0 %*	*0.8 %*	*0.6 %*	*0.8 %*
5 % SF	*1.5 %*	*0.5 %*	*0.4 %*	*0.5 %*
10 % SF	*1.0 %*	*0.3 %*	*0.2 %*	*0.3 %*
20 % FA	*1.2 %*	*0.4 %*	*0.3 %*	*0.4 %*
w/b 0.30				
100% CEM I	*2.2 %*	*1.0 %*	*0.8 %*	*1.0%*
5% SF	*1.6 %*	*0.6 %*	*0.5 %*	*0.6 %*
10% SF	*1.2 %*	*0.4 %*	*0.3 %*	*0.4 %*
20 % FA	*1.4 %*	*0.5 %*	*0.4 %*	*0.5 %*

*Chloride threshold levels vary extensively in field exposed concrete exposed to the air, as a consequence of the varying microclimate at the steel surface. As a consequence the chloride threshold level depends on the cover thickness and on the physical bonding between concrete and reinforcement. The chloride threshold levels are only valid for "macro crack free" concrete with a maximum crack width of 0.1 mm and a minimum cover of 25 mm. The data are not valid for calculations of the initiation time in cracked concrete with crack widths > 0.1 mm.

5. ENVIRONMENTAL ZONES

The environmental exposure to concrete structures in different exposure situations can be divided into different classes depending on the aggressiveness of the environment. This has been done in the Danish concrete standard, where four environmental classes is used: Passive, Moderate, Aggressive and Particular aggressive environmental class.

If moisture and chloride is present the environmental class is defined as aggressive or particular aggressive.

In Danish outdoor climate frost action also happens, which means that concrete in structures must be frost-resistant, if exposed to frost in a water-saturated condition during construction or in function.

The chloride-containing marine environment and the road environment can be subdivided into a number of local classes, while the chloride exposure is depending on the part of the structure. The distance to the waterline or the lane is one of the most important parameters. When striving towards an economical design of a structure one can group the individual structural parts/sections in different local environmental classes.

An appropriate division into local environmental classes, which is relevant in both marine environment and road environment, is given below. Besides, some examples on structural parts belonging to each local environmental class are stated. The purpose of this grouping is to exemplify the number of different chloride exposures, which can be seen on one structure. Among other things, the division is appropriate when planning inspection on a structure, while it for many (especially smaller) constructions will be too detailed as a paradigm for division into different environmental classes with varying covers and/or concrete qualities.

1. *Road environment*

a) The "wet" road environment, i.e. structural parts, which are able to "see" the sky and which are subjected to direct rain. ***Wet splash (WRS):*** The distance to the traffic is less than 4 m e.g. edge beams.

b) The "dry" road environment, i.e. structural parts, which are placed below a bridge deck and due to this not able to "see" the sky and not subjected to direct rain, but only to traffic splash**.** ***Dry splash (DRS):*** The distance to the traffic is less than 4 m e.g. pillars.

c) The region outside the borders mentioned above. ***Distant road atmosphere (DRA):*** The wet or the dry environment where the distance to the traffic is more than 4 m e.g. noise shelters or parts of the structure high above road level.

Marine environment

a) Submerged structures ***(SUB)*** placed below level -3 m with respect to the lowest minimum water level, e.g. caissons.

b) Structures placed in the splash zone ***(SPL)***, here defined as being above level -3 m with respect to the lowest minimum water level and below level +3 m with respect to the highest maximum water level, e.g. bridge pier shafts.

c) Structures placed in the atmosphere ***(ATM)*** above level +3 m with respect to the highest maximum water level, e.g. bridge piers and the underneath of decks on marine bridges.

6. ESTIMATION FORMULAS

An approach similar to that made by Frederiksen et al. [1997] is used in order to make semi–objective estimates for the threshold concentrations.

The values in Table 3 can be approximated by a formula of the type:

$$C_{\mathrm{cr}} = k_{\mathrm{cr},\,env} \times \exp\left(K \times \mathrm{eqv}\left(w/c\right)_{\mathrm{cr}}\right) \qquad (1)$$

A multiple regression analysis performed on the data in Table 3 is used to quantify the parameters. Based on that equation (1) is changed into (2) as follows:

$$C_{\mathrm{cr}} = k_{\mathrm{cr},\,env} \times \exp\left(-1.5 \times \mathrm{eqv}\left(w/c\right)_{\mathrm{cr}}\right)[\%\text{ mass binder}] \qquad (2)$$

The constants of (2) are given in Tables 4, 5 and 6.

Table 4. The constant $k_{cr,\,\mathrm{env}}$ *in (2) for the road environment.*

Environment: Constant:	Wet Road environment Splash (WRS)	Dry Road environment Splash (DRS)	Distant Road Atmosphere (DRA)
$k_{\mathrm{cr},\,env}$	1	1.25	1.25

Table 5. The constant $k_{cr,\,\mathrm{env}}$ *in (2) for the marine environment.*

Environment: Constant:	Submerged marine environment (SUB)	Marine environment Splash (SPL)	Marine Atmosphere (ATM)
$k_{\mathrm{cr},\,env}$	3.35	1.25	1.25

Table 6. The activity factors for corrosion initiation in the road environment to be used when calculating the eqv $(w/c)_{cr}$ *ratio in (2).*

Activity factor	Silica fume	Fly ash
k	-4.7	-1.4

The quality of the suggested formula (2) can be visualised graphically by plotting the values of Table 3 versus the values obtained by calculations according to (2), cf. Figure 4 for the road environment and in Figure 5 for the marine environment.

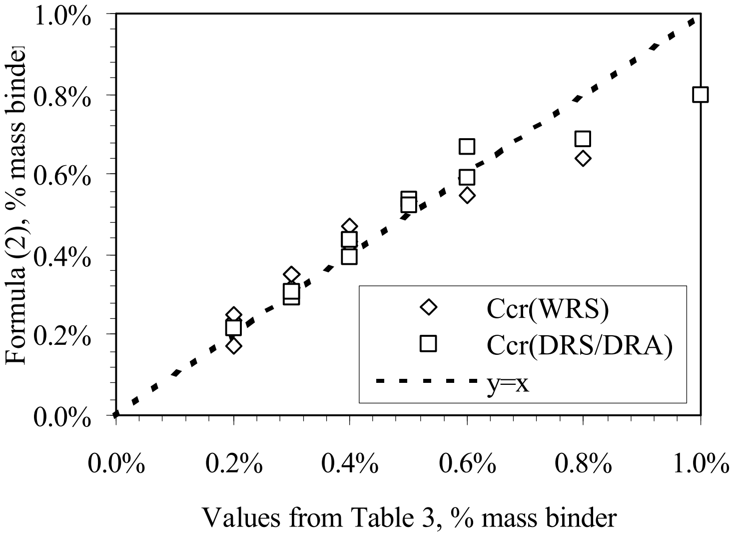


Figure 4. Plot of the values of Table 3 versus the values obtained by calculations according to the "model". The estimates of C_{cr} are seen to be in a fairly good agreement with the original data (Table 3, which are estimates too). ***Road Environment.***

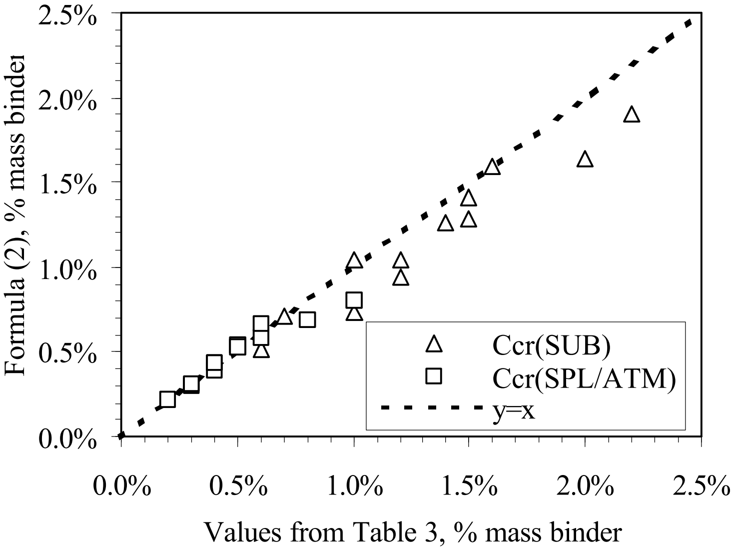


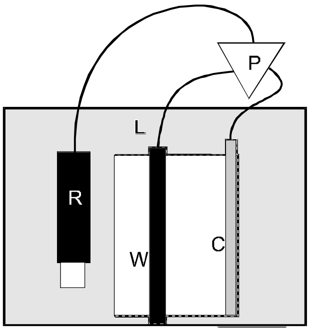
Figure 5. Plot of the values of Table 3 versus the values obtained by calculations according to the "model". The estimates of C_{cr} are seen to be in a fairly good agreement with the original data (Table 3, which are estimates too). ***Marine environment.***

7. ATTEMPT TO DEVELOP A RELIABLE TEST METHOD

An ongoing NORDTEST project with the scope of developing/defining a test method for determination of chloride threshold values has been prolonged until mid 2000. Below some preliminary considerations and results are presented.

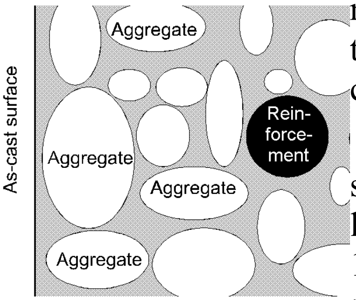
The first objective was to decide what is understood when using the term “Chloride Threshold Value”. The end-user of the result from such an experiment wants to know at what chloride concentration in the concrete the corrosion will initiate.

Many threshold value determinations have been concentrating on measuring the chloride concentration in the near by region of the steel reinforcement bar, e.g. by sophisticated techniques capable of measuring the chloride concentration exactly at the steel-concrete interface. This is in principle correct. All results from experiments trying to do this more or less precisely have the disadvantage that they are difficult to translate into reliable values that are useful for the end-user and maybe also difficult to compare with results from similar investigations.



The most simple and reliable technique to determine the corrosion on-set is to hold the steel electrode potentiostatically controlled during the exposure, cf. figure. By “continuously” monitoring the current needed (1-3 μA) to maintain the passive steel at a certain potential, e.g. 0 mV vs. SCE, it can very precisely be monitored when the on-set of the corrosion appears because the current needed will rise one or two orders of magnitude.

By combining the above experience it is in fact natural to define the chloride threshold value as the concentration of chloride in the infinitesimal layer where the concrete cover of the reinforcement is measured at the time where the corrosion on-set is established. Therefore a new approach is introduced: *At the time of on-set of corrosion the chloride concentration in the undisturbed bulk concrete is measured at the depth of the reinforcement.* In other words: It is *not* considered what the chloride concentration is at the concrete-steel interface because that is not an interesting value for the end-user. The concentration to consider is that appearing in the *undisturbed* bulk concrete near to the steel.



Experience shows that the outermost surface layer (against a mould) of about 10 mm is not like the *undisturbed* bulk concrete. Having passed 10 mm from the as-cast surface the concrete becomes more homogeneous, i.e. the cement paste volume becomes more constant with depth. The phenomenon behind this is the fact that large aggregate particles will only tend to touch the mould in a “point” so that the cement paste concentration in the surface is close to 100%. This changes dramatically when moving inward in the concrete. Therefore it is natural to regard the concrete cover from the surface to the reinforcement as an inhomogeneous material consisting of three layers with different characteristics:

1. The surface layers where a plane typically governs the position of the aggregate.
2. The bulk layers where the position of the aggregate is random.
3. The rebar layers where a circle typically governs the position of the aggregates.

To avoid disturbances in the chloride concentration measurement from the layers 1 and 3 above one needs to be away from disturbing bodies in the concrete. Experience from chloride diffusion experiments says that 10 mm are sufficient to eliminate this problem. Therefore the specimen for the chloride threshold experiment now is designed to provide the needed space, cf. the sketch on the following page.

7.1 Test method

The project must result in a detailed description of how to perform the test. Therefore the test method is being prepared along with defining more and more of the test.

7.2 Test parameters

As quite a lot of experience exists of how to perform the corrosion on-set measurement the effort is at this stage concentrated on finding/defining:

- The level for the potential
- The needed cover thickness
- To determine the experimental scatter in-lab and between-labs.

To different levels of potentials were applied: 0 mV vs. SCE and +350 mV vs. SCE. Three cover thicknesses, 5 mm, 10 mm and 15 mm are used in one laboratory. Six specimens of three concrete mixes are to be tested in each laboratory.

7.3 Types of concrete investigated

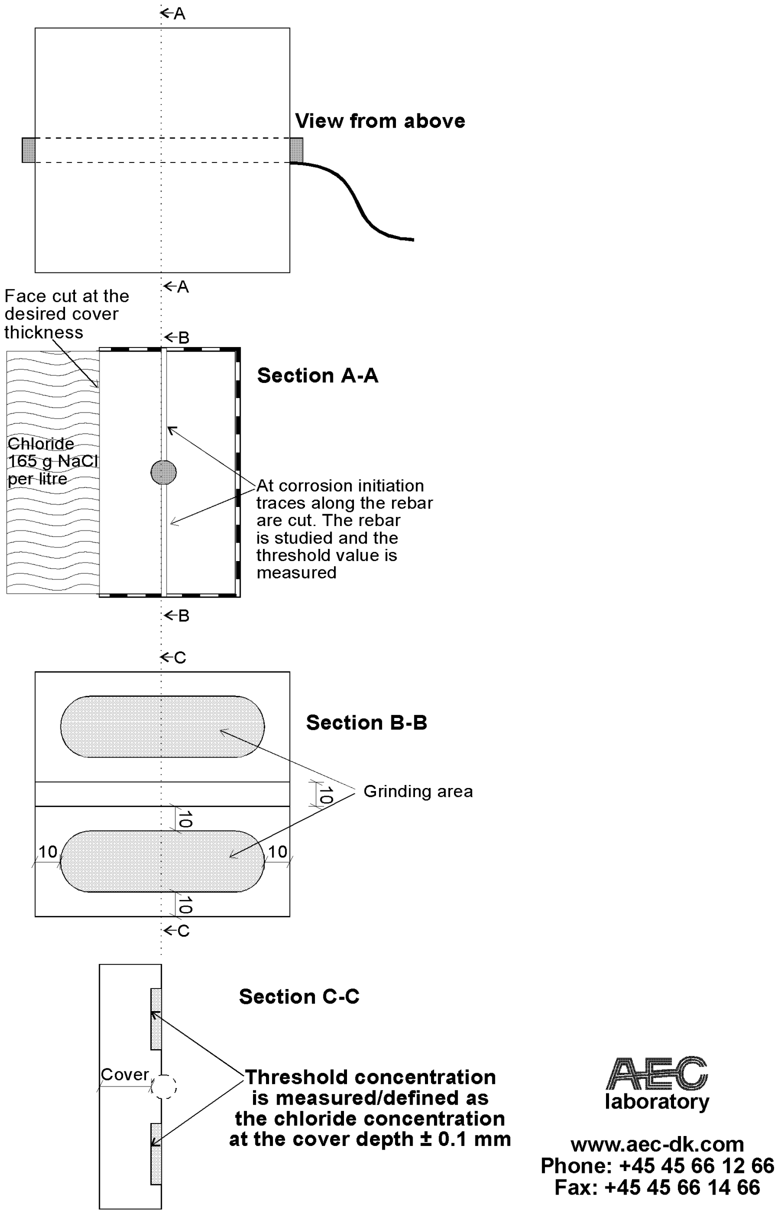
Three types of concrete have been cast for the experiments. The only difference between the concrete is the type of cement. Three Danish cement types were chosen:

a) Low alkali sulphate resisting Portland Cement, CEM I 42.5
b) Rapid Hardening Portland Cement, CEM I 52.5
c) Portland Filler Cement, Cem II 52.5

Those cement types represent the most commonly used cements on the Danish market and at the same time comparison with other European countries is possible.

Three concretes were manufactured so that they had the same water-cement ratio (0.45), the same paste volume (27 %), the same aggregate size distribution, the same initial slump (45 mm) and the same natural air-content (1.5 %). The maximum aggregate size is 16 mm.

Principle for defining and measuring the chloride threshold value for corrosion initiation in concrete



7.4 Some preliminary results

Until now only very few and rather uncertain data have been obtain from the tests. Problems have arisen with the protection of the steel concrete interface where the specimens are submerged into the sodium chloride solution. The results do however give some kind of information as seen below.

Only data from the specimens having a concrete cover of 5 mm have been obtained.

In the period from 2 to 5 months of exposure it was decided to stop five specimens in the test because the current needed to maintain the potentiostatic potential at +350 mV vs. SCE was too high, i.e. above 0.030 mA. The measured chloride concentrations at the rebar level are shown in Figure 6 together with some results from an earlier investigation carried out on mortar bars, at a potentiostatic potential at 0 mV vs. SCE and with a cover thickness of 16 mm.

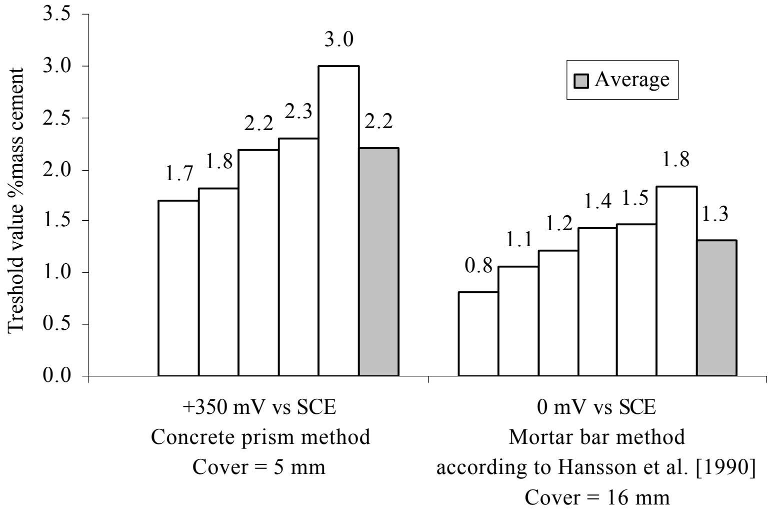


Figure 6. Results from the Nordtest project (left) versus results from some previous measurements (right). Both sets of data are from concrete with Danish Low Alkali Sulphate Resisting Cement (CEM

8. SUMMARY AND CONCLUSION

The established table and formula for estimation of chloride threshold values in different environments and for different concrete compositions is a step forward. Now threshold values depend logically on the type of exposure and type of concrete involved. By establishing a common test method for the determination of threshold values hopefully, more data and experience will sprout up.

Only few results from the ongoing experiments exist at this moment (ultimo March 2000). From the formula given above, the expected level of the chloride threshold value in the experiment can be found as follows:

The type of exposure in the test is constant submersion, but the potentiostatically controlled “artificial potential” may make the set-up comparable to the marine atmosphere (or any of the four environments SPL, ATM, DRS or DRA). The threshold value in the test is therefore assumed to be 0.64% mass cement or 0.094 % mass concrete (354 kg cement / 2385 kg concrete) if the test environment is similar to one of the four environments.

If instead the test environment is more like “SUB” the expected threshold value is 1.71% mass cement or 0.25% mass concrete. The preliminary results indicate that the test environment more likely is comparable to the submerged condition. This again indicates that the applied potential at or above 0 mV vs. SCE in the test has little or no effect in providing a situation similar to that of an aerated condition in a real structure.

An observation that supports the indication of the little relevance of the applied positive potential in the potentiostatic test is the finding of higher threshold values at higher potentials, cf. Figure 6.

The preliminary results also indicate that it should be “safe” to use a concrete cover of 5 mm when this is obtained by cutting away the excess cover after the concrete has hardened.

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