

**SINTEF Building and Infrastructure** Gro Markeset and Øystein Vennesland (editors)

# Critical chloride content in reinforced concrete

COIN workshop, 5-6 June 2008, Trondheim, Norway

COIN Project report 6 - 2008



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P4 «Operational service life design»

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## Preface

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This workshop has been carried out within COIN - Concrete Innovation Centre - one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfil this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %).

For more information, see [www.coinweb.no](http://www.coinweb.no)

Tor Arne Hammer  
Centre Manager



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## Introduction

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The COIN workshop was held in June 5–6, 2008, at the Norwegian University of Science and Technology NTNU in Trondheim, Norway. It focused on critical chloride content (chloride threshold value) in reinforced concrete with emphasis on techniques for determining critical chloride contents and its relevance for practice.

This report includes the abstracts and the foils presented at the workshop.

The programmes for the two days and the list of participants are shown below.

### Workshop programme:

#### *Day 1, Thursday 5 June, 2008*

08.00 – 08.50	Registration
0850 – 09.00	Welcome by <b>Tor Arne Hammer</b> (Project Manager of COIN)
09.00 – 10.00	<b>Chris Page:</b> Importance of the steel-concrete interface with regard to corrosion initiation in the presence of chloride. Discussion
10.00 – 11.00	<b>Josef Tritthart:</b> Pore solution of concrete. The equilibrium of bound and free Discussion
11.00 – 12.00	<b>Luca Bertolini:</b> Depassivation of steel in case of pitting corrosion - detection techniques for laboratory studies. Discussion
12.00 – 13.00	<b>Lunch</b>
13.00 – 14.00	<b>Maria Cruz Alonso:</b> Chloride threshold values in the literature. Discussion
14.00 – 15.00	<b>Bernhard Elsener:</b> Chloride sensors in concrete - accuracy and long term stability. Discussion
15.00 – 16.00	<b>Ueli Angst:</b> Laboratory experiments for detecting critical chloride content in reinforced concrete. Discussion
16.00 – 17.00	<b>Rob Polder:</b> Relationship between electrical concrete resistivity and critical chloride content. Discussion
20.00	Dinner at Grenaderen restaurant

#### *Day 2, Friday 6 June, 2008*

09.00 – 10.00	<b>Joost Gulikers:</b> Critical considerations regarding laboratory research on the critical chloride content in reinforced concrete. Discussion
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10.00 – 11.00	<b>Gro Markeset:</b> Critical chloride content and its influence on service life predictions. Discussion
11.00 – 12.00	<b>Tang Luping:</b> A field study of critical chloride content in reinforced concrete with blended binder Discussion
12.00 – 13.00	<b>Lunch</b> in Realfagsbygget
13.00 – 14.00	<b>John Miller:</b> Reference material for calibrating chloride analysis of hardened concrete Discussion
14.00 – 15.00	<b>Jens Frederiksen:</b> On the need for more precise threshold values for chloride initiated corrosion in design, repair and maintenance of reinforced concrete structures - a consultant's view. Discussion
15.00	Closing the workshop

**The workshop participants:**

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## **1 Initiation of chloride-induced corrosion**

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### **“Initiation on Chloride-induced Corrosion of Steel in Concrete: Role of the Interfacial Zone”**

*Chris L. Page*

*University of Birmingham*



## **Initiation of Chloride-induced Corrosion of Steel in Concrete: Role of the Interfacial Zone**

C L Page  
University of Birmingham

Given that some of the basic phenomena associated with the passivity of ultra-pure iron in aqueous solutions of NaOH and KOH are still incompletely understood (1,2), it would be surprising, to say the least, if the same were not true for aspects of the electrochemical behaviour of reinforcing and prestressing steels in concrete. One of the many reasons for this is that pre-existing layers of mill-scale or rust, which may or may not be present on the metal surface prior to its embedment in a concrete structure, are liable to affect the ease with which passivation and depassivation will occur, as has been noted by many researchers (3-12). Such layers of mixed oxides and hydrated oxides of iron, whose natures and thicknesses depend on features of the alloy composition, the manufacturing process and the vagaries of storage, are notoriously variable and difficult to characterise. Fortunately, however, the high pH values of the pore solutions formed during cement hydration (13) are normally sufficient to induce passivation of embedded steel, as is evident from the noble potentials ( $> 200 \text{ mV}_{\text{SCE}}$ ) that are typically observed for reinforcing bars embedded in atmospherically exposed concrete structures which have not become significantly contaminated by chlorides or carbonation.

When studying the influence of variables, related to concrete composition, methods of manufacture, environmental exposure conditions etc, that affect the corrosion behaviour of steel in concrete exposed to chloride ingress, it has usually been necessary to start by cleaning the metal surface because particular samples of bars in their ‘as-received’ or ‘pre-rusted’ conditions are not representative or reproducible. For this reason, laboratory research has mainly been undertaken with steel bars, which have been cleaned by grit blasting or similar methods and then degreased and stored in dry air until use. An example of this kind of investigation, performed at Aston University (6,14), examined relationships between the corrosion responses of embedded steel bars and pore solution compositional features (determined at various depths corresponding to the bars) within Portland cement concrete slabs of different types that were exposed for 6, 12 and 24 months to external chloride solutions (5% NaCl). The main objective of the work was to elucidate the circumstances leading to depassivation of steel that had been allowed to form a stable passive layer over a long period in well-made laboratory specimens of concrete.

The results demonstrated that, in concrete specimens, which were as free as possible from macroscopic defects (voids, cracks, crevices etc) at the surfaces of embedded bars, no significant corrosion of passive steel was induced until the concentration of free chloride ions in the pore solution near the bars exceeded that of free hydroxyl ions by a factor of at least 3 times and, in some cases, as much as 20 times. These ratios of free  $[\text{Cl}^-]/[\text{OH}^-]$  were far higher than those that had previously been found (15,16) to cause depassivation of steel in bulk alkaline electrolytes of the same pH range as existed within the concrete at depths corresponding to the bars when depassivation was

recorded. This difference was believed to be due mainly to the buffering effect of a layer of cement hydration products deposited in intimate contact with the passive film on the embedded steel. It was concluded that a significant cause of the much lower tolerance to chloride exhibited by steel bars in reinforced concrete structures exposed to deicing salt (17) was the presence of macroscopic defects which disrupt the integrity of the layer of hydration products deposited at the steel-concrete interface. Another contributory factor was suggested to be the variable surface condition of the steel reinforcement prior to its embedment in site-produced concrete (6).

More recently, researchers at the University of South Florida (8) have compared the behaviour of steel bars, which were either sandblasted or not cleaned prior to being immersed in bulk aqueous solutions maintained at various constant pH values (12.6, 13.3 and 13.6). After passivation had been induced, increased concentrations of chloride were progressively introduced into the solutions and it was shown that: (i) the sandblasted steel bars were more tolerant to chloride than the mill-scaled or pre-rusted bars, (ii) the critical ratios of free  $[Cl^-]/[OH^-]$ , at which depassivation of the bars was observed, increased with increasing solution pH value (being  $\ll 1$  at pH 12.6 and  $\gg 1$  at pH 13.6). These results are relevant to reinforced concrete exposed under conditions where chloride ingress is not accompanied by significant reduction in the pore solution pH. They do not, however, account for the very high ratios of free  $[Cl^-]/[OH^-]$  that were found around many of the passive steel bars in the earlier work at Aston University. While the bulk internal pH values of the Aston specimens were originally in the expected range for Portland cement concretes of w/c 0.5 ( $13.6 > pH > 13.3$ ) the leaching of free hydroxyl ions that accompanied chloride ingress was found to have reduced the pH to about 12.5 and resulted in free  $[Cl^-]/[OH^-]$  ratios  $> 10$  at depths corresponding to several of the bars that were found to be maintained in a passive condition (6,14).

That the high tolerance to chloride-induced pitting sometimes exhibited by steel in concrete exposed to the ingress of chloride ion might be due, in part, to the chemical buffering action of solid hydration products deposited in the interfacial zone was first suggested as long ago as 1975 (18) and discussed in further detail in subsequent papers of similar vintage (19,20). In the original publication (18) it was noted that previous workers had found that voids at the interface were almost invariably the positions at which corrosion of steel reinforcement and prestressing tendons takes place (21) and that measures which promote homogeneity of the interfacial zone, such as application of a slurry of neat Portland cement paste to the steel before embedding it in concrete, were known to be effective in reducing the risk of chloride-induced corrosion (22). At that time, plain Portland cements were generally used for structural applications in saline environments and rather limited evidence was available concerning microstructural features of interfacial zones with embedded steel, the most relevant contribution cited in (18) being a paper by Moreau in which scanning electron microscopy (SEM) had been used in secondary electron imaging mode to examine fracture surfaces of interfaces formed above and below horizontal reinforcing bars (23). Moreau's work, which was published in French, showed that segregated portlandite (CH) crystals of varying morphology were a major component of the interfacial regions and demonstrated that, when compared with the relatively compact layers of hydration products deposited over the upper surfaces of the bars, the undersides were characterised by more porous, open-

textured zones with much larger single crystals of CH that had grown in the relatively thick solution-filled spaces formed by collection of bleed water beneath the bars.

Several subsequent investigations involving the use of secondary electron imaging SEM have confirmed the presence of segregated CH-enriched interfacial zones at clean mild steel or stainless steel fracture surfaces that had been in contact with Portland cement pastes, mortars and concretes (24-34) though the morphology and degree of orientation of the CH have been found to vary, as has the distribution of C-S-H and other hydrate phases that have been identified. These different observations seem to suggest that Portland cements of differing compositions, which give rise to significant differences in the early development of their pore solution chemistry (13), may form somewhat distinct sequences of solid hydration products via the through-solution routes that are generally believed to give rise to early-stage microstructural development at interfaces. Until recently, only very limited studies of interfacial zones formed at pre-corroded reinforcing steel appear to have been reported (35,36), mainly no doubt because of the difficulties involved in producing the required steel substrates with well-characterised surfaces that are adequately reproducible and representative.

Although the examination of simply debonded surfaces by SEM is a useful method for qualitative characterisation of steel/concrete interfaces, the approach is not capable of providing quantitative compositional data for reasons that have been discussed in relation to the study of aggregate/concrete interfaces (37). Production of polished sections cut perpendicular to the interfaces concerned is necessary for this purpose and these sections can be analysed at moderately high resolution by means of back scattered electron imaging SEM. There are, however, problems of specimen preparation that must be avoided as the surfaces concerned have to go through a number of potentially damaging processes (viz. drying, evacuation and resin impregnation followed by several stages of mechanical polishing) throughout which the possibility of introducing artefacts exists. Research undertaken at the University of Leeds, has attempted to overcome some of these experimental problems and a recent paper (38) has provided quantitative data derived from a back scattered electron imaging SEM study of interfaces formed between concrete made from a particular ordinary Portland cement and 9mm diameter ribbed reinforcing bars that were embedded vertically or horizontally. Prior to embedment, the surface of the steel was either 'as-received' (with rust and millscale present) or, in some cases, cleaned by wire brushing. Among other things, the results reported appear to show that, for the particular materials and conditions studied: (i) vertical steel bars had interfacial zones of higher CH content and higher porosity than the bulk cement matrix; (ii) for horizontal bars marked differences between the upper and lower interfaces were found with higher porosity on the undersides, thus confirming the observations of Moreau (23); (iii) cleaned steel bars had higher levels of CH at the interface than uncleaned bars after long periods of embedment.

Some remaining problems of specimen preparation for quantitative analysis by back scattered electron imaging SEM probably need further consideration if efforts are to be made to resolve the detailed effects of cement compositional variables on interfacial zone microstructure. This may be of some interest in view of the increasing use now being made of cements with high levels of supplementary cementitious materials (SCMs) that react with CH. If the aim is to develop new cements, which can offer enhanced protection to embedded steel under conditions of exposure to chlorides, there may have to

be compromises between: (i) maintaining the buffering capacity at appropriately high pH values while excluding hydrates with easily released bound chloride from the interfacial zones, and (ii) limiting the bulk chloride penetrability of the materials concerned.

At the macroscopic level, deleterious effects of water-filled voids formed beneath reinforcing bars owing to the collection of bleed water at the steel-concrete interface have been confirmed to lead to enhanced corrosion susceptibility in the presence of chloride so measures aimed at improving mix stability (resistance to bleeding and sedimentation) may offer a practical way of improving chloride tolerance (39). Similarly, deleterious effects of entrapped air voids at the steel-concrete interface have been investigated and a number of suggestions made as to how their impact on chloride threshold levels for reinforcing steel in concrete might be reduced (40). It appears, however, that the threshold chloride content is not dominated by any one parameter which can provide a simple index for comparing different types of concrete. It is actually a function of interacting variables that include, but are not limited to, factors affecting the potential of the steel and those influencing the composition of the interfacial zone. It therefore remains a challenging task to propose rapid laboratory tests that might be used reliably to predict chloride threshold values for reinforced concrete structures made from non-traditional materials when experience of long-term performance under field exposure conditions is unavailable. Exposure tests of reasonably long duration, performed under conditions that are as realistic as possible, are believed to be necessary for this purpose (41).

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## **2 Pore solution of concrete**

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### **“Pore solution of concrete: the equilibrium of bound and free chloride”**

*Josef Tritthart*

*Graz, University of Technology*



## Pore solution of concrete: The equilibrium of bound and free chloride

J. Tritthart

### 1. Introduction

It was in the second half of the fifties of the last century that it became apparent that chlorides may trigger corrosion in the steel reinforcements of concrete. However, during subsequent investigations carried out in order to determine which chloride content is harmless and which is not, greatly differing limit values were obtained. In Austria, a limit value of 0.4 % chloride related to the cement content of concrete was introduced as an assessment criterion. This amount of chloride was considered to be harmless because based on test results it could be concluded that cement is able to bind “firmly and permanently” up to 0.4% of chloride [1]. The author of this paper was alerted to the question of chloride-induced corrosion of reinforced concrete in the second half of the seventies. Checks on road bridges in Austria in which the author was involved (such checks were performed more and more frequently in the aftermath of the collapse of Vienna’s Reichsbrücke in 1976) quite often showed areas of clearly enhanced chloride content but no signs of steel corrosion. This prompted the author to start investigations of his own.

The threshold value of 0.4% and all the other threshold values of cement-based materials found in literature were based on the total chloride content of the concrete related to the cement mass. As only the unbound chloride which remains dissolved in the pore solution can interact with the protective layer on the steel surface, possibly destroy it and initiate corrosion, the investigations focused on the chloride concentration of the pore solution after binding and the factors of influence. For this, pore solution was pressed out of hardened cement pastes which were prepared i) with the addition of a chloride salt or ii) free of chloride but the chloride was added subsequently via diffusion. That way it should be found out whether there were differences in chloride binding between samples which contained chloride from the very beginning and samples into which chloride penetrated after hardening.

### 2. Chloride binding in cement when added during sample preparation

For sample preparation, the chloride salt was dissolved in the mixing water before mixing. The fresh pastes, which had been mixed with a spoon, were filled into containers supported by frames that could be turned. After filling, the containers were tightly closed and turned over night to avoid sedimentation. Then the samples were wrapped in plastic bags and stored at 20°C until testing. Then, pore solution was partly squeezed out and analysed.

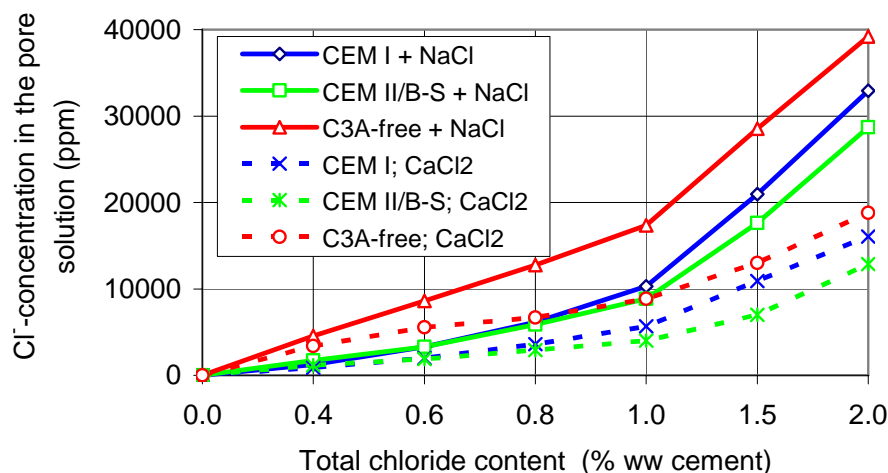


Figure 1: Cl<sup>-</sup>-concentration of the pore solution versus total chloride content

Figure 1 shows the influence of total chloride content. It can be seen that the chloride concentration in the pore solution increased continuously with increasing total chloride content and that there were differences depending on the type of cement as well as on the chloride salt added. Most chloride was bound by the CEM II/B-S followed by the CEM I and least chloride was bound by the C<sub>3</sub>A-free sulphate-resisting cement. The continuous increase of the Cl<sup>-</sup>-concentration in the liquid phase indicates that besides chemical binding adsorptive binding took place as well. Were only chemical binding to occur, the equilibrial Cl<sup>-</sup>-concentration of the pore water should have remained relatively constant as long as clinker phases such C<sub>3</sub>A, which are able to bind the chloride chemically, were present and would increase rapidly if these components reacted. To verify the influence of C<sub>3</sub>A available for chloride binding, the sulphate content of cement was increased in various steps. The more C<sub>3</sub>A reacted with the sulphate and formed ettringite ("trisulfate"; 3CaO·Al<sub>2</sub>O<sub>3</sub>·3CaSO<sub>4</sub>·32H<sub>2</sub>O) the more gypsum was added and the less C<sub>3</sub>A remained available for chloride binding. As expected, the Cl<sup>-</sup>-concentration of the pore solution increased with increasing sulphate content of the cement but remained approx. constant from a C<sub>3</sub>A/SO<sub>4</sub><sup>-2</sup>-ratio of 3 upwards.

Figure 1 shows furthermore that the Cl<sup>-</sup>-concentration of the pore solution was higher when NaCl was added than when CaCl<sub>2</sub> was added. This is in agreement with findings described by other authors [2, 3]. However, it was surprising that the influence of the added chloride salt was even higher than that of the type of cement. This can be explained by the changes in the OH<sup>-</sup>-concentrations of the pore solution.

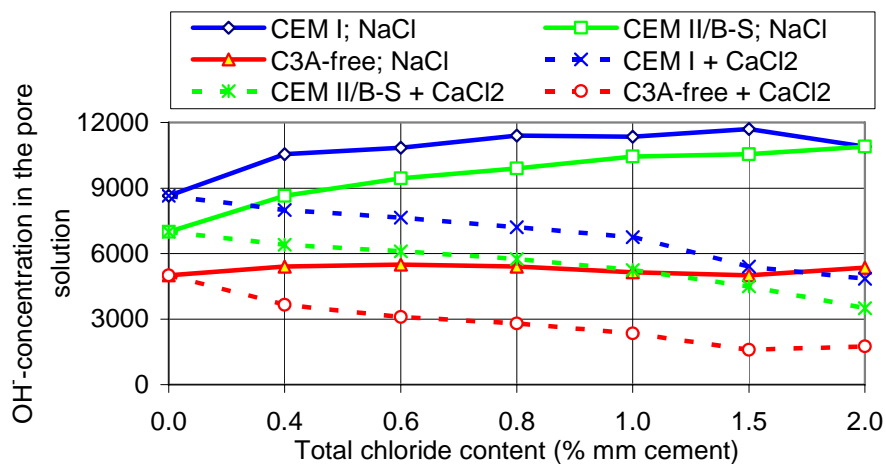


Figure 2: OH<sup>-</sup>-concentration of the pore solution versus total chloride content

As can be seen from Figure 2, the hydroxide concentration increased with the use of NaCl but decreased with CaCl<sub>2</sub>. The reason for the difference in OH<sup>-</sup>-concentration of the pore solution between samples containing NaCl and CaCl<sub>2</sub> is that at the high pH-values of the pore solution calcium is insoluble (contrary to sodium) and precipitates as Ca(OH)<sub>2</sub>. Therefore the OH<sup>-</sup>-concentration of the pore solution is reduced the more the higher the amount of CaCl<sub>2</sub> [4, 5]. Further studies with the use of other chloride compounds which reduce the OH<sup>-</sup>-concentration in the same way as CaCl<sub>2</sub> does (MgCl<sub>2</sub>, HCl) showed that practically the same amount of chloride was bound as was the case with CaCl<sub>2</sub>. When mixtures of chloride compounds were added which affected the OH<sup>-</sup>-concentration of the pore solution differently (NaCl/CaCl<sub>2</sub>, etc.), the more chloride was bound (the less was the Cl<sup>-</sup>-concentration of the pore solution) the more the OH<sup>-</sup>-concentration decreased. The effect of the OH<sup>-</sup>-concentration of the liquid phase on chloride binding was also found when the alkali content of the cement was reduced by washing out before sample preparation.

Although the found correlations strongly suggest adsorptive binding of chloride and hydroxide apart from chemical binding, definite evidence can hardly be furnished due to overlapping equilibria and the complex overall situation. This can explain why the addition of silica-fume, which reduces the OH<sup>-</sup>-concentration of the liquid phase, was found to cause an increase in chloride binding in one study but a decrease in another study (different cements, different types of silica fume, etc.) [5, 6].

### 3. Subsequently added chloride

To examine the binding of chloride added subsequently by diffusion, chloride-free cement slabs of 1 cm thickness and w/c-ratios of 0.5 and 0.7 were used [4, 5]. After 28 days of hardening, the slabs were immersed in chloride-containing solutions until no further chloride uptake occurred so that the chloride concentration was practically the same in the pore solution and in the storage solution. The slabs were immersed in storage solutions with different OH<sup>-</sup>-concentrations, namely in saturated Ca(OH)<sub>2</sub> (pH-value: 12.5), 0.1 m NaOH (pH-value: 13.0) and 0.5 m NaOH (pH-value: 13.7). Five different Cl<sup>-</sup>-concentrations were used. From time to time the Cl<sup>-</sup>-concentration of the storage solution was measured and used-up chloride replenished. That way the Cl<sup>-</sup>-concentrations were kept more or less constant over the whole test period. Pore solution was pressed out after about 1 year in order to be sure that a state of equilibrium had been reached and that the composition of the pore solution had become equal to that of the storage solution. Only then the final determination of the total chloride content of the samples was carried out. The results are shown in Figure 3.

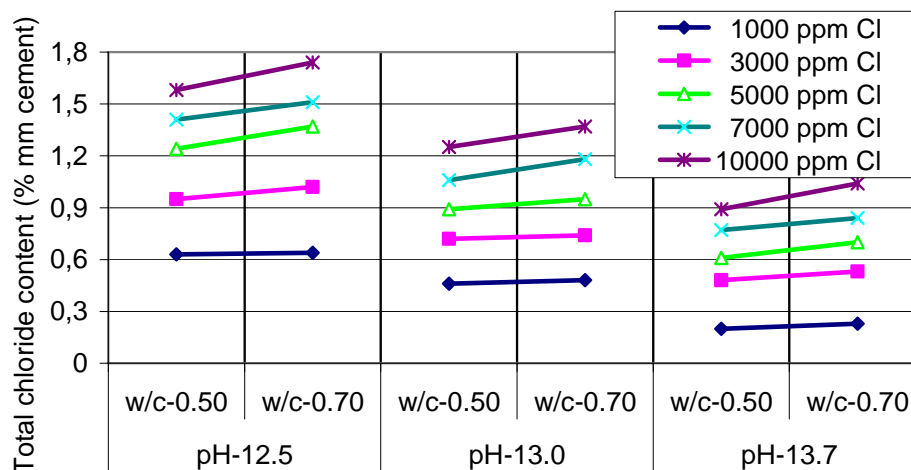


Figure 3: Chloride uptake of cement pastes immersed in chloride solutions

As can be seen from Figure 3 the higher the chloride concentration of the storage solution was the more chloride was taken up by the hardened cement. The pH-value played a major role as well; the higher the pH-value, the less chloride was taken up. The influence of the w/c-ratio on the other hand was rather insignificant - samples with a w/c-ratio of 0.7 took up slightly more chloride than the ones with a w/c-ratio of 0.5. The calculation yielded that, as in the samples prepared with the addition of chloride, the proportion of bound chloride remained practically the same regardless of the w/c-ratio. Thus the influence of the w/c-ratio was almost exclusively due to the different content of pore water in the samples.

### 4. Conclusions

The results showed that chloride is not bound in absolute quantities but rather in dependence on an equilibrium which is established between solids and the liquid phase. The state of equilibrium and thus the residual chloride concentration depends on the composition of the cement as well as on the chemistry of the pore solution and in particular on its OH<sup>-</sup>-concentration.

As regards the assessment of the corrosion risk, the results showed that the Cl<sup>-</sup>-concentration of the pore solution varied between samples made of the same cement and containing a total chloride content of 1% between 2600 ppm and 23000 ppm. Other results showed that the Cl<sup>-</sup>/OH<sup>-</sup>-ratio of the pore solution - which is often mentioned to be a better indicator for the assessment of corrosion risk [7] - increased at a given total chloride content with decreasing w/c-ratio which, however, is inconsistent with practical experience. These results illustrate very well that a certain total chloride content alone is not a suitable criterion for the assessment of corrosion risk.

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Pore solution of concrete  
The equilibrium of bound and free chloride







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Trondheim 05-06 June 2008



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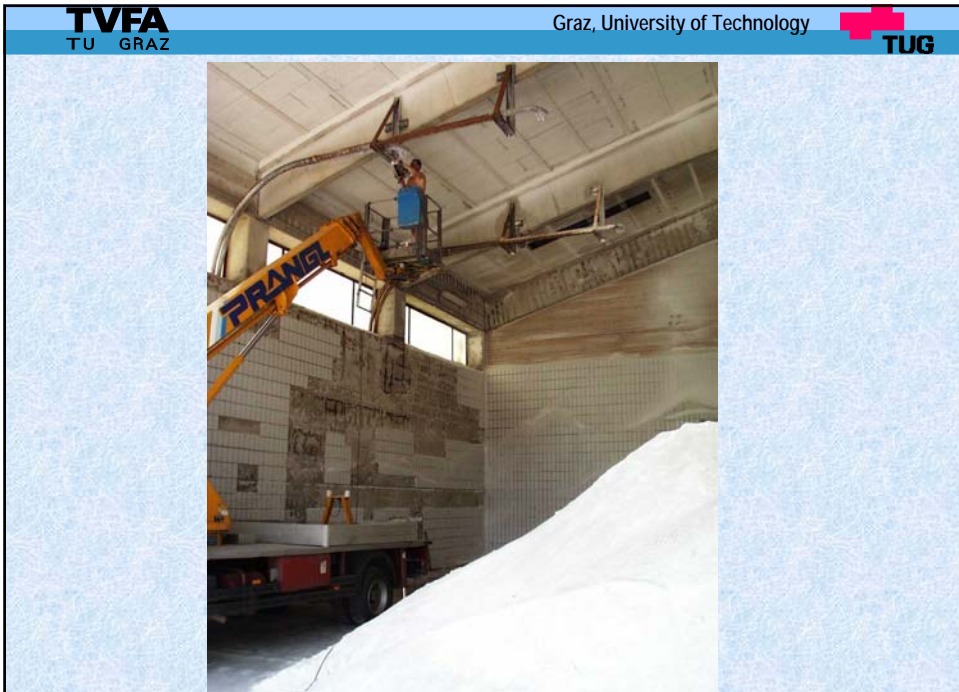
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1.  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  ( $\text{C}_3\text{A}$ ) +  $3\text{CaSO}_4$  +  $32\text{H}_2\text{O}$   $\rightarrow$   $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$   
(Ettringite; "Trisulfate")
  
2.  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  +  $\text{CaCl}_2$  +  $10\text{H}_2\text{O}$   $\rightarrow$   $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$  (Friedel salt)
  
3.  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$  (Ettringite) +  $2[3\text{CaO}\cdot\text{Al}_2\text{O}_3]$   $\rightarrow$   
 $3[3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}]$  (Monosulfate)

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**Threshold values (empirically; total chlorid)**

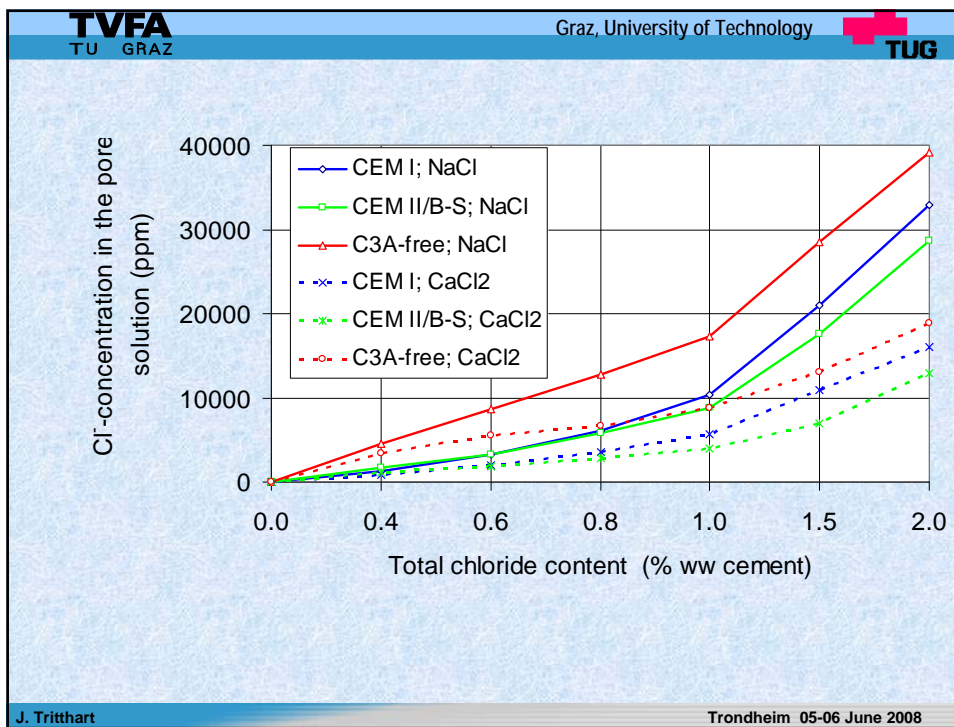
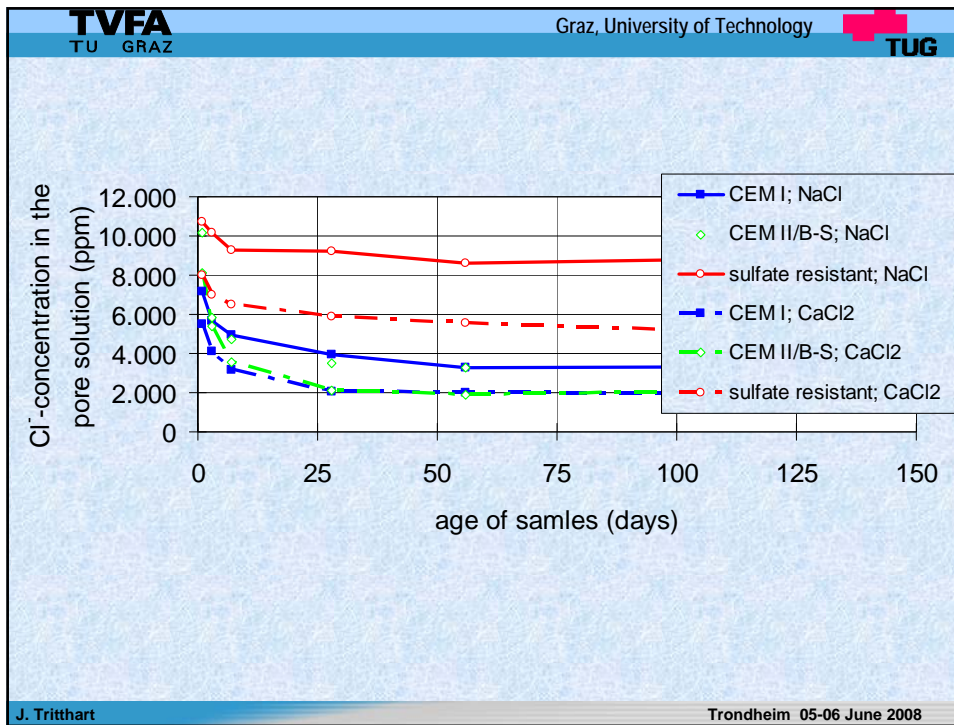
Related to mass of concrete	Related to mass of cement	author
---	2% $\text{CaCl}_2$ (~ 1,3 Cl <sup>-</sup> ) at a concrete porosity of max. 9,5 Vol-% and a min. Cover of $\geq 1,5$ cm	Tomek und Vavrin (1961)
---	0,2% Cl <sup>-</sup>	Clear & Hay (1973)
approx. 1 lb Cl <sup>-</sup> /yd <sup>3</sup> (= approx. 0,59 kg Cl <sup>-</sup> /m <sup>3</sup> ; = ca. 0,02%)	---	Stratfull et al (1975)
500 ppm Cl <sup>-</sup>	---	Stewart (1975)
0,028% Cl <sup>-</sup> at 330 kg PC/m <sup>3</sup> and a water soluble Cl <sup>-</sup> -content of 75%; 0,051% Cl <sup>-</sup> at 390 kg PC/m <sup>3</sup> and a water soluble. Cl <sup>-</sup> -content of 50%	---	OECD-Road Research Group (1976)
---	2% $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ (= ~1,3% Cl <sup>-</sup> ; at dense concrete; otherwise less)	Working group „Monoliet“ (1976)
---	0,4% Cl <sup>-</sup>	Everett et al (1980)
---	1,0% - 1,5% Cl <sup>-</sup> (at dense concrete; otherwise less)	Lukas (1980)

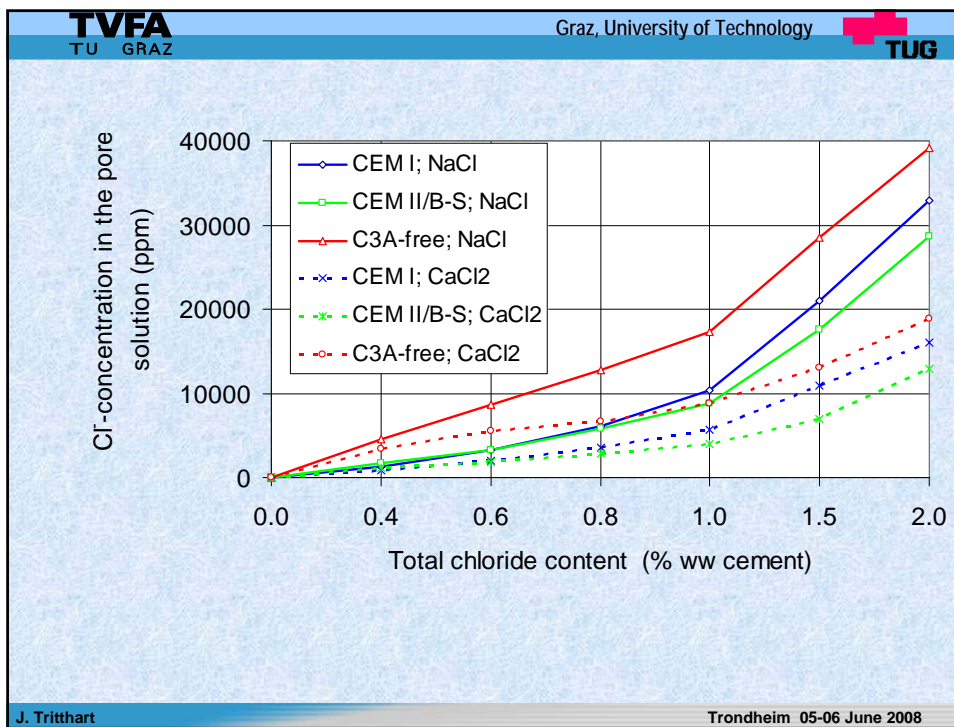
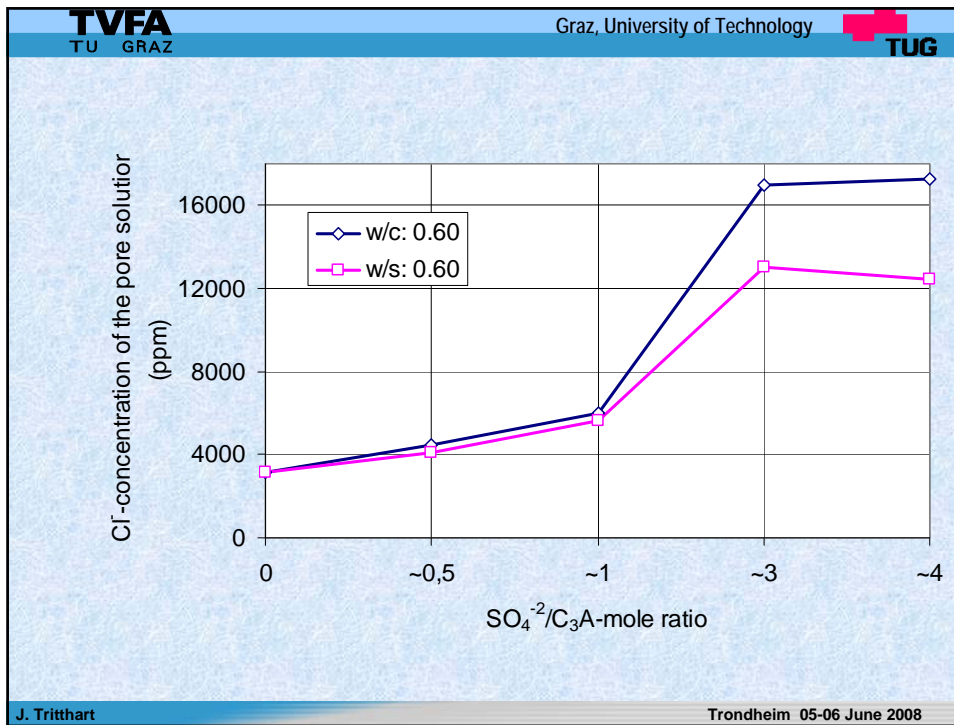
J. Tritthart Trondheim 05-06 June 2008

**critical Cl<sup>-</sup>-concentration and Cl<sup>-</sup>/OH<sup>-</sup> - ratio**

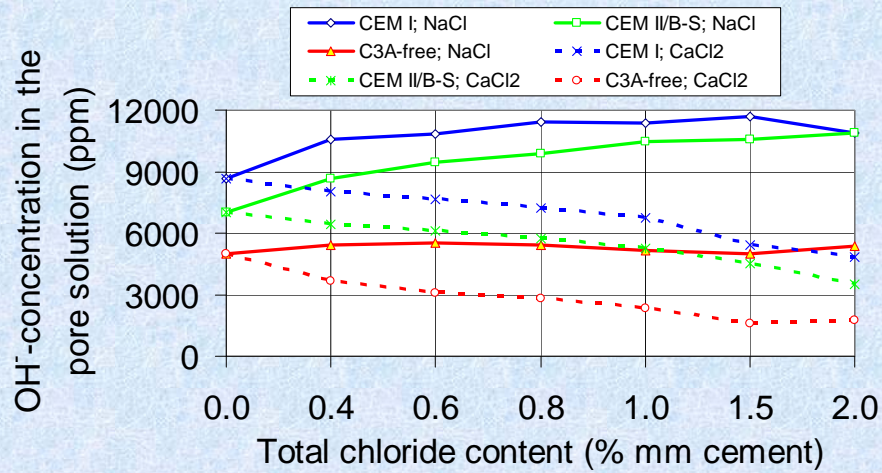
alkaline solutions	concrete/ mortar	author
<35 ppm CaCl <sub>2</sub>	up to 3.1 % CaCl <sub>2</sub>	Bäumel a. Engell (1959)
Cl <sup>-</sup> /OH <sup>-</sup> - ratio ≤ 0,6 in pH-range 11,6 – 13,2	---	Hausmann (1967)
in pH-range 11,5 – 13,5: pH = n log C <sub>Cl</sub> + K	---	Gouda (1970)
Cl <sup>-</sup> /OH <sup>-</sup> - ratio: 0,3	---	Diamond (1986) [from data of Gouda]
---	Cl <sup>-</sup> /OH <sup>-</sup> - ratio: ~ 3	Lambert, Page u. Vassie (1991)
---	Cl <sup>-</sup> /OH <sup>-</sup> - ratio: ~ 5	unknown, quoted by Goni and Andrade (1990)





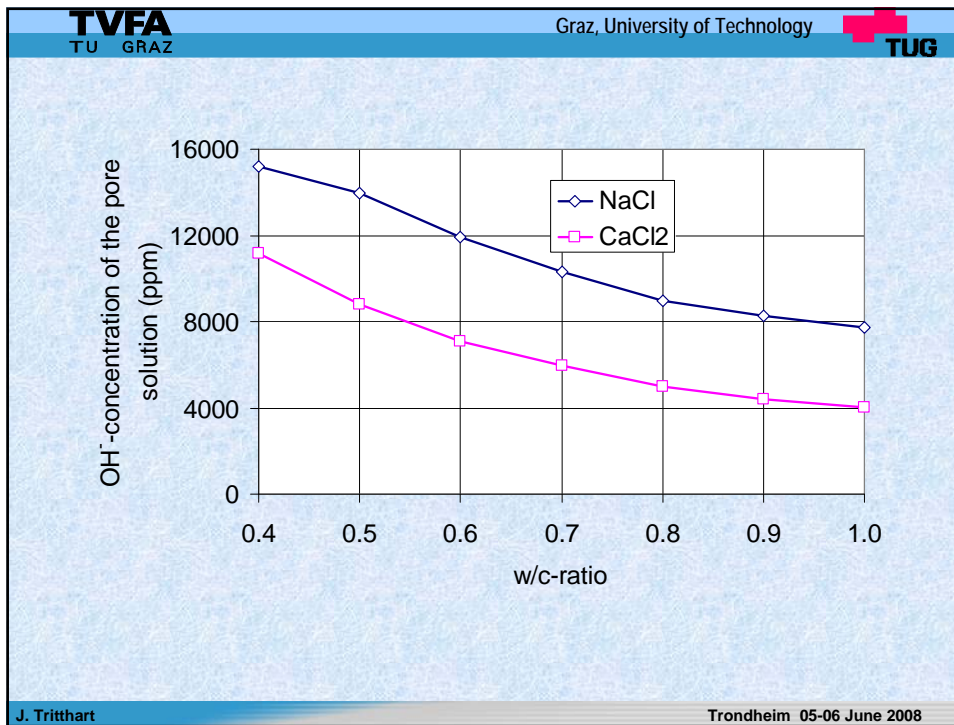
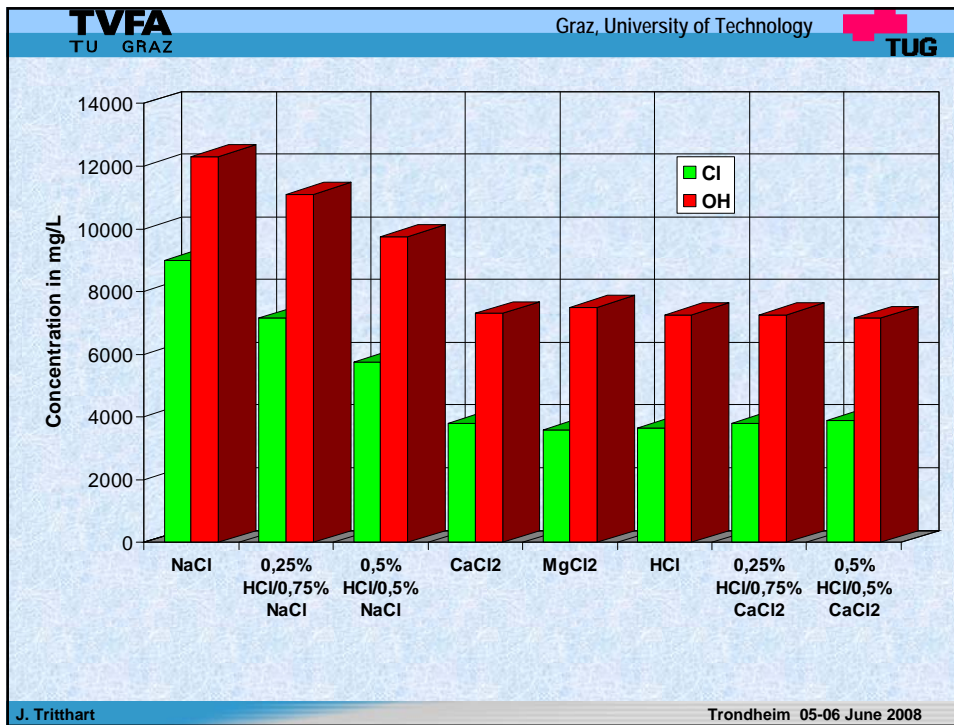


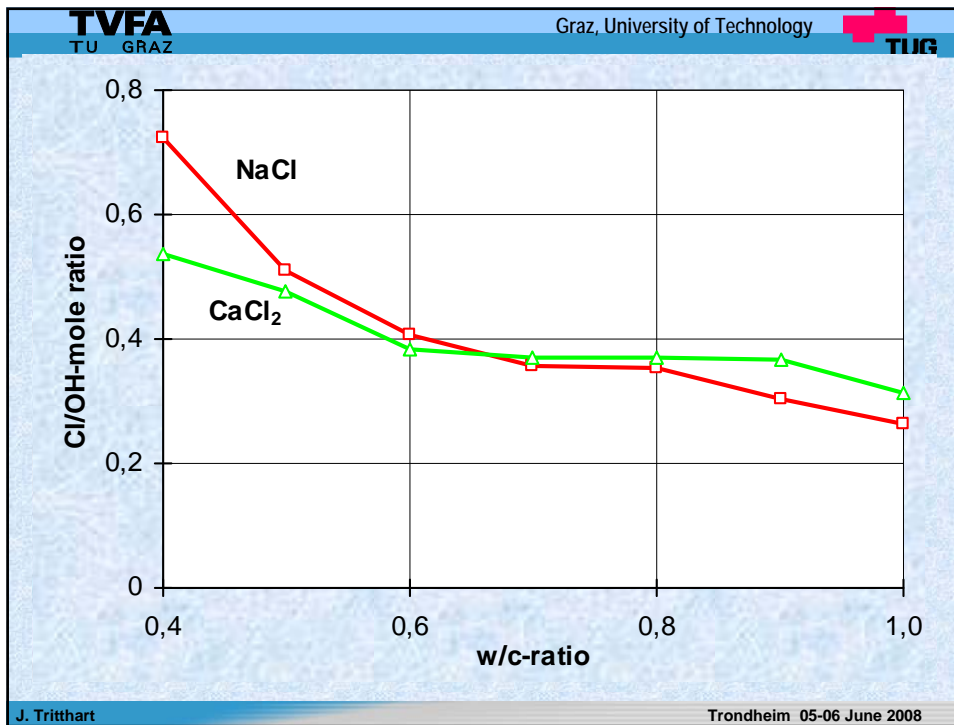
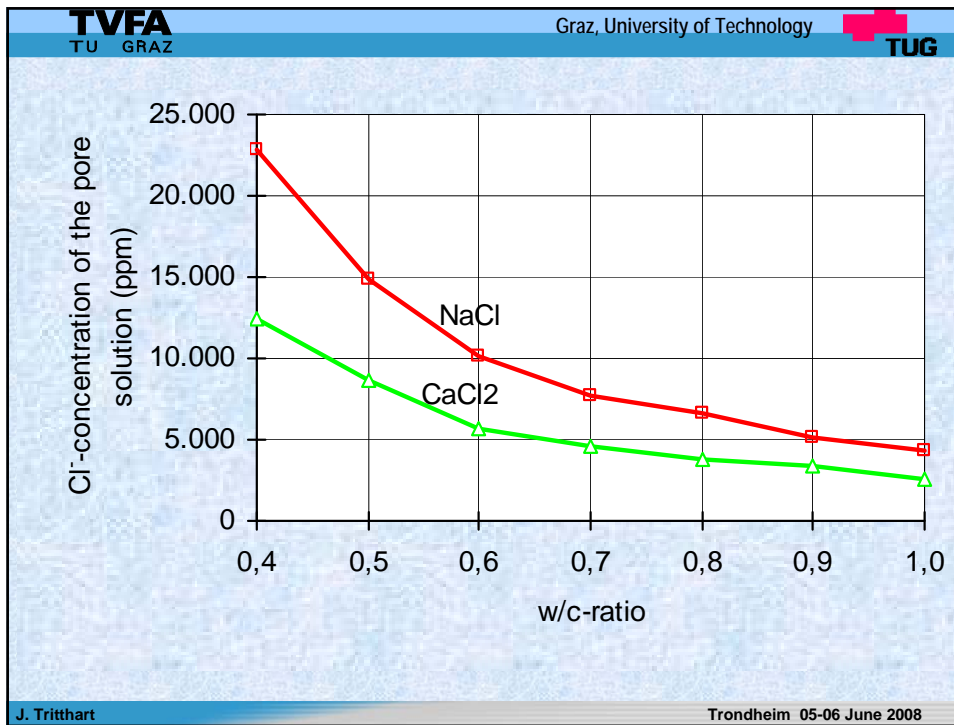


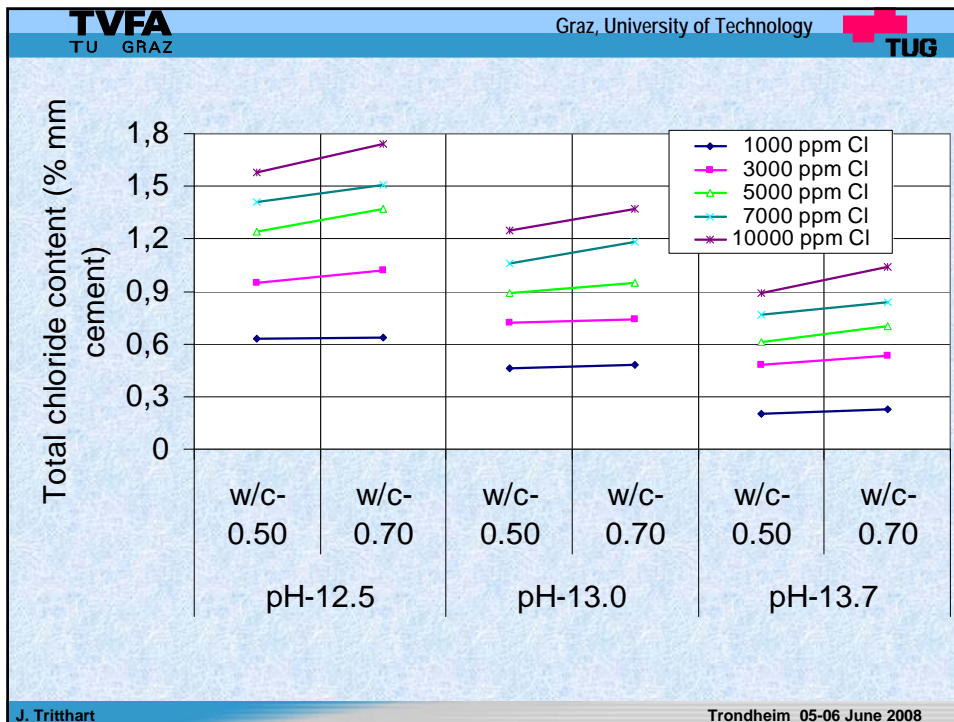
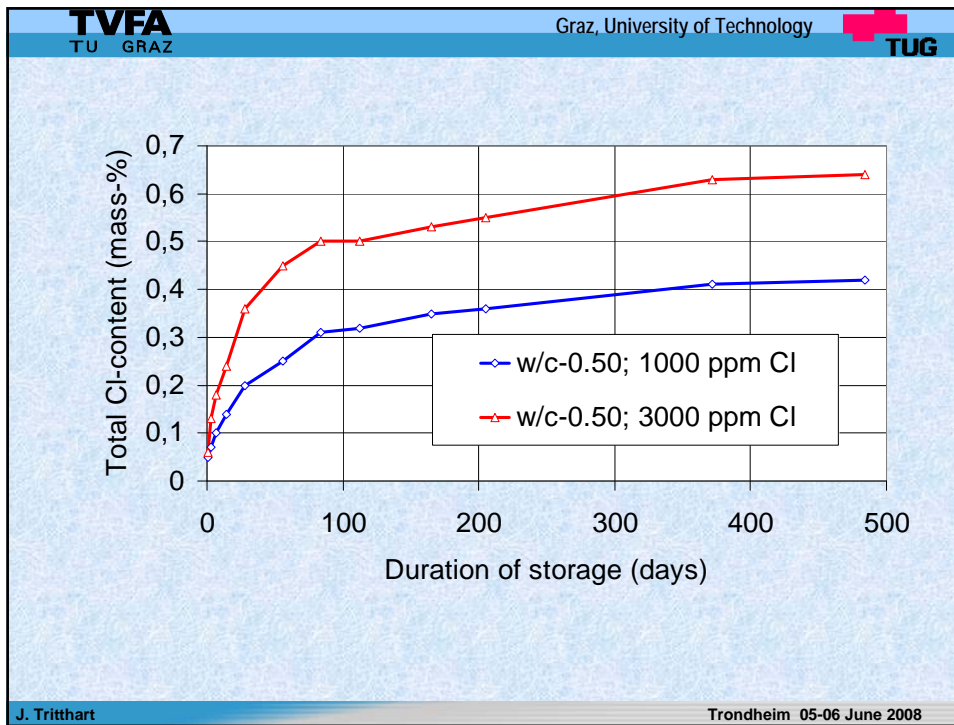


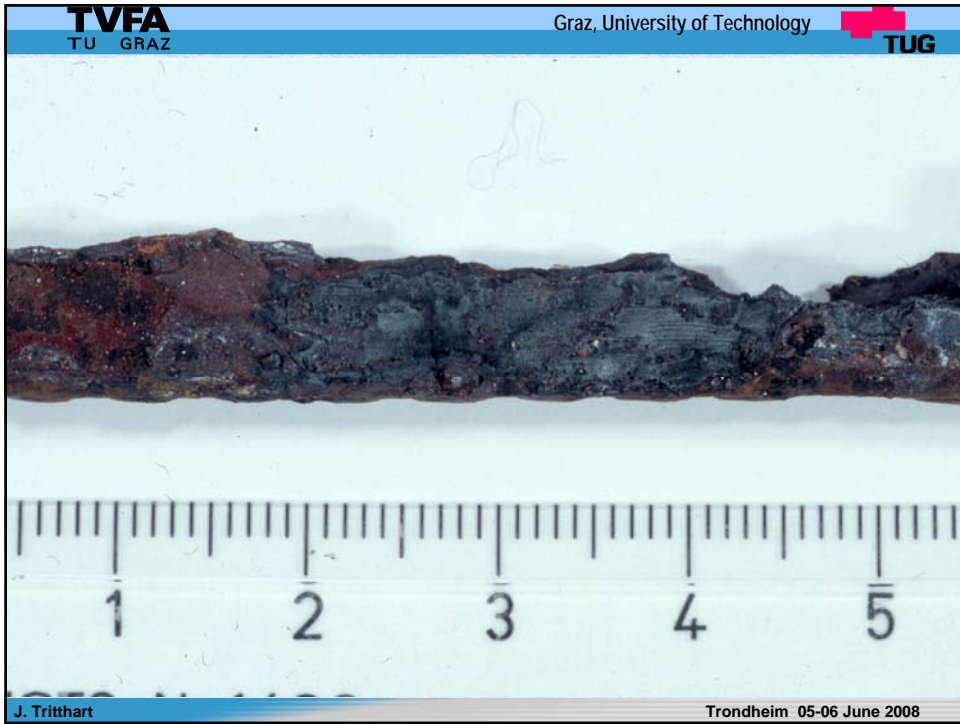
- $[Ca^{+2}] \cdot [OH^-] \cdot [OH^-] = 5.47 \cdot 10^{-6}$
- $[Ca^{+2}] = 5.47 \cdot 10^{-6} / [OH^-]^2 = 5.47 \cdot 10^{-6} / 10^{-2} =$
- $5.47 \cdot 10^{-4} \text{ mole } Ca^{+2}/l = \sim 22 \text{ ppm}$

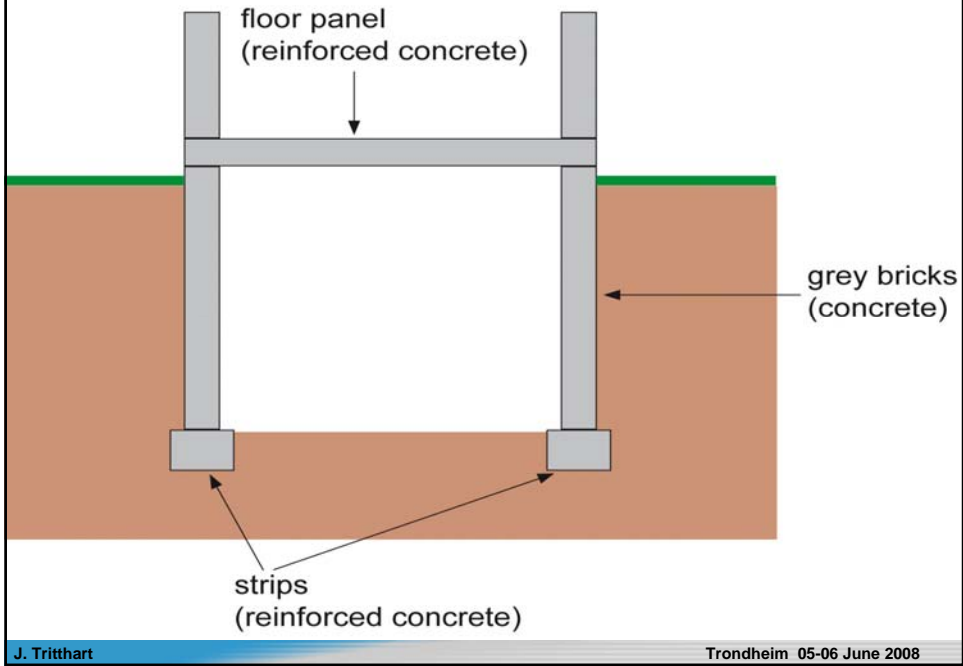
$Ca^{+2}$ -ions are not soluble at high pH-values and precipitate as  $Ca(OH)_2$













### **3 Depassivation of steel in case of pitting corrosion**

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## **Depassivation of steel in case of pitting corrosion – Detection techniques for laboratory studies**

*Luca Bertolini*

*Politecnico di Milano*





## **Depassivation of steel in case of pitting corrosion Detection techniques for laboratory studies**

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According to Tuutti’s model, methods for the design of durability of reinforced concrete structures exposed to marine environments or the action of de-icing salts, divide the service life into an initiation period, during which chloride ions penetrate the concrete cover and initiate pitting corrosion, and a subsequent propagation period during which corrosion leads to a limit state affecting the serviceability or safety of the structure. In order to calculate the initiation period, the chloride threshold ( $Cl_{th}$ ), i.e. the minimum amount of chloride ions that is required to breakdown the passive film and initiate pitting corrosion, should be defined. If the penetration of chloride as a function of depth ( $x$ ) and time ( $t$ ) is known  $Cl(x,t)$ , the chloride threshold may be measured as the chloride content detected at the depth of the bars when corrosion initiates, i.e.:

$$Cl_{th} = Cl(x = c, t = t_i)$$

where  $c$  is the thickness of the concrete cover and  $t_i$  is the initiation time.

The definition of  $Cl_{th}$  is quite complex for several reasons. First of all, pitting corrosion initiation is a stochastic phenomenon that is influenced by a great number of parameters.  $Cl_{th}$ , in principle, should be defined through probability distributions that take into account the effect of those parameters. However, such an approach would require a huge amount of experimental data which is in practice impossible to collect. Statistical analysis are available in the literature only with regard to the effect of single influencing parameters. Furthermore, experimental details, such as the way chlorides are introduced in the concrete (e.g. added to the mixing water or penetrated by diffusion or migration) or the means of measuring the chloride content (e.g., total acid soluble chlorides expressed by mass of cement or free chlorides from pore expression expressed as concentration in solution) may have a large influence on the resulting value of the chloride threshold. The technique used to detect the corrosion initiation of steel may also have a remarkable effect on the chloride threshold.

Since there are no standardized methods for the evaluation of the chloride threshold, as well as for the detection of corrosion initiation, a large variety of techniques has been used by different researchers. Indeed, even the definition of the initiation of pitting corrosion is not simple. In fact, an initial phase where breakdown of the passive film alternate to repassivation at incipient anodic sites is followed by a permanent active corrosion stage, where sustained pit propagation takes place. From a practical point of view, it is often assumed that corrosion is initiated when an anodic current density above a certain threshold (i.e.  $1 \text{ mA/m}^2$ , corresponding to roughly  $1 \text{ }\mu\text{m/year}$  of average corrosion rate) is reached.

The electrochemical behaviour of steel in chloride contaminated concrete can be described through the polarization curve depicted in Figure 1 (proposed by Pourbaix), that plots the anodic current density (measuring the rate of steel dissolution) as a function of the steel potential, in concrete with a given content of chloride ions. This figure shows, at low potential values, the passive range where the corrosion rate is negligible. Pitting corrosion initiates when the potential of the steel is above a pitting potential ( $E_p$ ), which is a function of the chloride content, but also of several other parameters (pH of the pore solution, temperature, microstructure and composition of the steel-concrete interface, composition and surface finishing of the steel bar, etc.). This means that, if the corrosion potential of the passive steel ( $E_{cor}$ ) is known,  $Cl_{th}$  can be defined as the amount of chloride that brings about a value of  $E_p$  equal to  $E_{cor}$ .

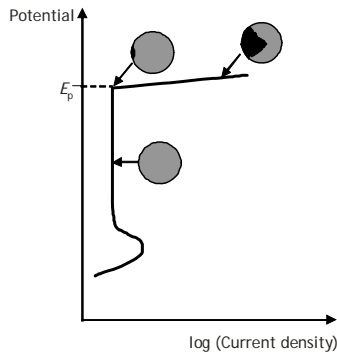


Figure 1 – Polarization curve of steel in chloride contaminated concrete and definition of the pitting potential  $E_p$ .

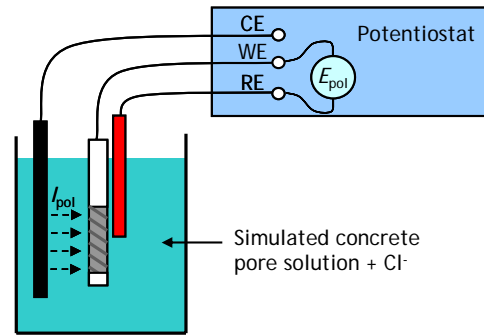


Figure 2 – Set up of tests in solution.

This presentation deals with the possible approaches used to detect depassivation of steel in relation to the definition of  $Cl_{th}$ . Firstly, tests in alkaline solutions that simulate the concrete pore liquid will be described. These are sometimes used to evaluate the resistance of steel to pitting corrosion, e.g. to compare different types of steel or the effect of preventative techniques (such as corrosion inhibitors). A steel specimen is immersed in the test solution, as depicted in Figure 2, and it is connected to a potentiostat that can impose a polarization potential ( $E_{pol}$ ) by means of a polarization current ( $I_{pol}$ ). Potentiodynamic polarization tests can be used to plot the polarization curve of steel with the aim of detecting  $E_p$ . By repeating the tests in solutions with varying concentration of chloride ions ( $[Cl^-]$ ), the relationship between  $E_p$  and  $[Cl^-]$  can be plotted and  $Cl_{th}$  can be extrapolated in correspondence of a reference value of  $E_{cor}$ . Potentiostatic polarization tests can be used, i.e. the potential of the steel is kept constant and, for instance, chloride are added step-wise until corrosion initiation is detected by a sharp increase in  $I_{pol}$ .

Tests on steel bars embedded in concrete (or mortar) specimens are generally considered to be more appropriate than solution tests for a quantitative evaluation of  $Cl_{th}$ . Specimens are exposed to chloride penetration (by ponding, wet-dry cycles, exposure to natural marine environments, migration, etc.) and the chloride content is measured at the depth of the steel bars at the time when corrosion initiation is detected. Alternatively, chlorides can be added to the concrete mix; although this approach is generally considered less appropriate, since the steel is not allowed to form a passive film in chloride-free concrete, it can drastically reduce the time of testing, especially when impervious concrete is considered. In this case, the chloride threshold can be detected by comparison of specimens with higher chloride contents where corrosion initiates and those with lower chloride contents where corrosion does not initiate. Corrosion initiation can be assessed by visual inspection, i.e. when macroscopic consequences of corrosion take place (e.g. cracking of concrete, loss of steel mass or cross section). However, corrosion can be detected only in a later stage and, if chlorides penetrate from the surface,  $Cl_{th}$  may be overestimated. Monitoring of electrochemical parameters, usually the corrosion potential and the corrosion rate (measured by means of the linear polarization technique), are often used in order to be able to detect corrosion initiation soon after it takes place (corrosion initiation of steel in concrete exposed to the atmosphere is normally accompanied by a sharp decrease in the corrosion potential and increase in the corrosion rate). Alternatively, the steel may be polarized potentiostatically and corrosion initiation may be detected by the increase of several orders of magnitude in the polarization current. Finally, depassivation may also be measured with macrocell tests (by potential difference or current flowing between passive and active steel).

Examples of different methodology utilized for the detection of depassivation, based on the above mentioned techniques will be shown during the presentation and advantages and limitations of test in solution will be addressed.



Politecnico di Milano

Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta"

COIN Workshop on  
*Critical chloride content in reinforced concrete*  
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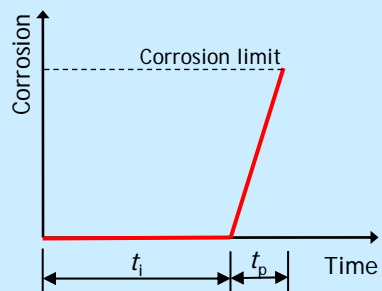
## Depassivation of steel in case of pitting corrosion Detection techniques for laboratory studies

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### Chloride induced corrosion

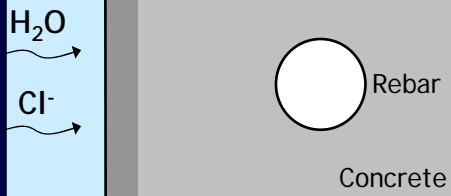
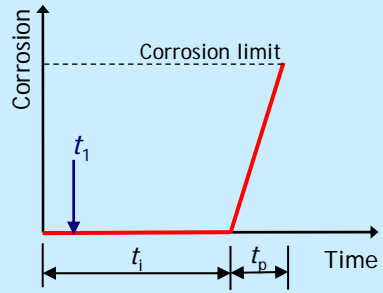
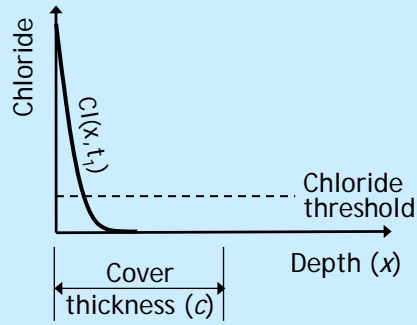


L. Bertolini. Depassivation of steel in case of pitting corrosion.  
Detection techniques for laboratory studies



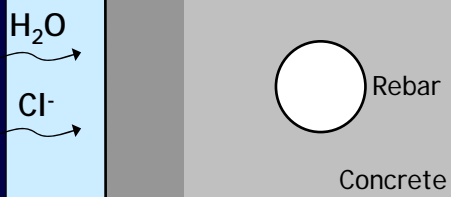
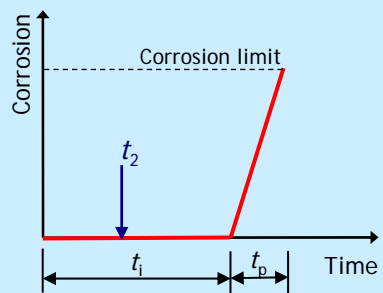
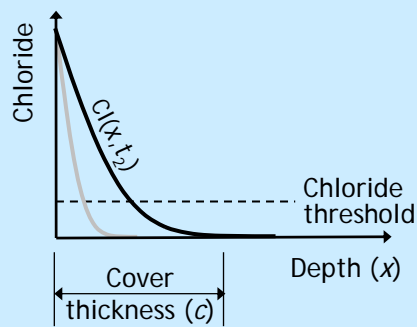
## Chloride induced corrosion

L. Bertolini - Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Chloride induced corrosion

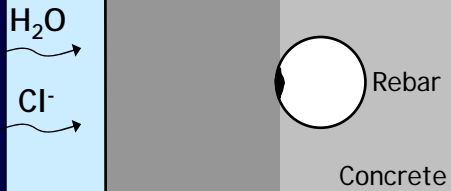
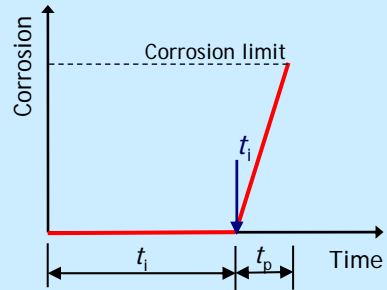
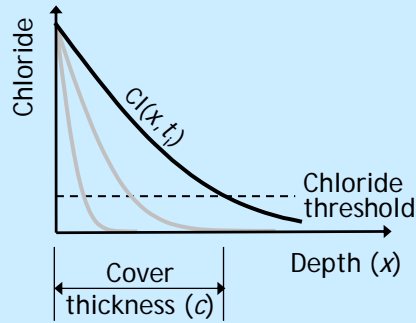
L. Bertolini - Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies





## Chloride induced corrosion

L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



$$Cl_{th} = Cl(x=c, t=t_i)$$

$t_i$  = time when  
corrosion "initiates"



## Chloride induced corrosion

L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies

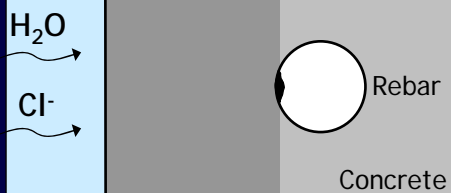
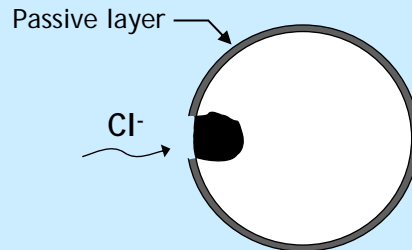
1) Depassivation/repassivation  
(incipient anodic site)

2) Permanent active corrosion



$$I_{cor} > 0.1 \mu A/cm^2 (\approx 1 \mu m/year)$$

(C. Andrade, COST 521 Final Report, 2002)



$$Cl_{th} = Cl(x=c, t=t_i)$$

$t_i$  = time when  
corrosion "initiates"



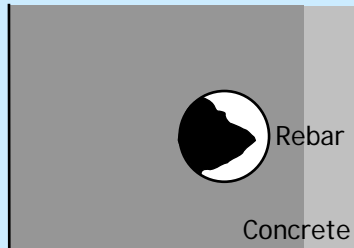
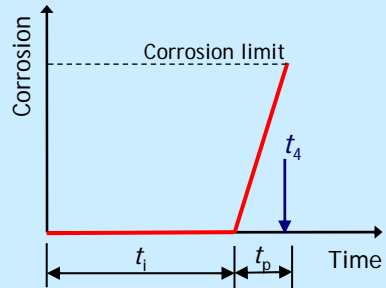
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- 1) Depassivation/repassivation (incipient anodic site)
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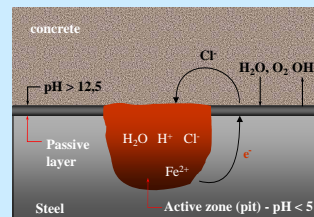
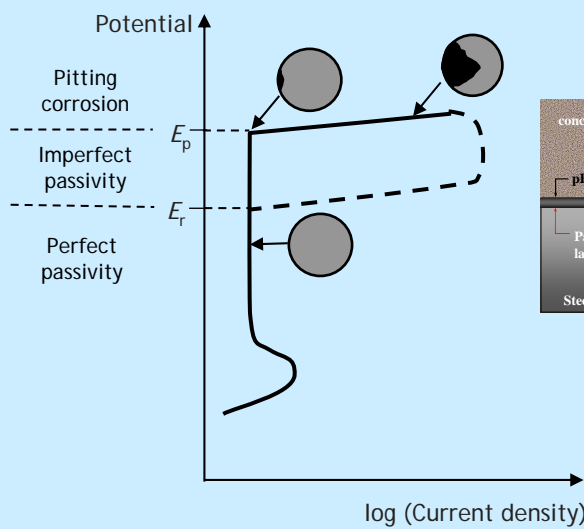
(C. Andrade, COST 521 Final Report, 2002)



L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Electrochemical behaviour of steel in concrete



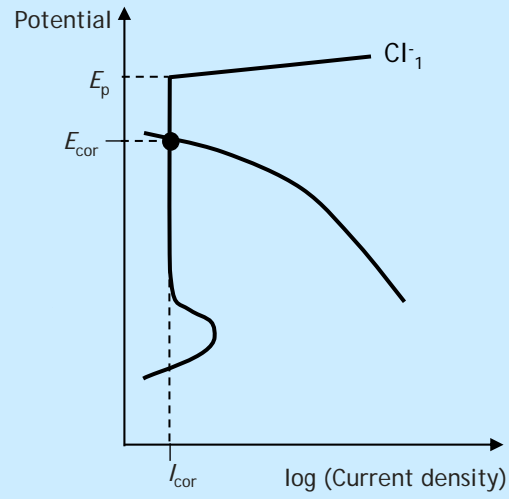
L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies

M. Pourbaix, Lectures on Electrochemical Corrosion, 1973



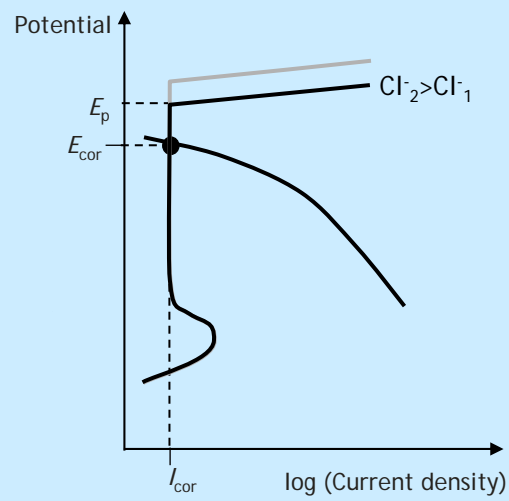
## Electrochemical behaviour of steel in concrete

L. Bertolini - Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Electrochemical behaviour of steel in concrete

L. Bertolini - Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies

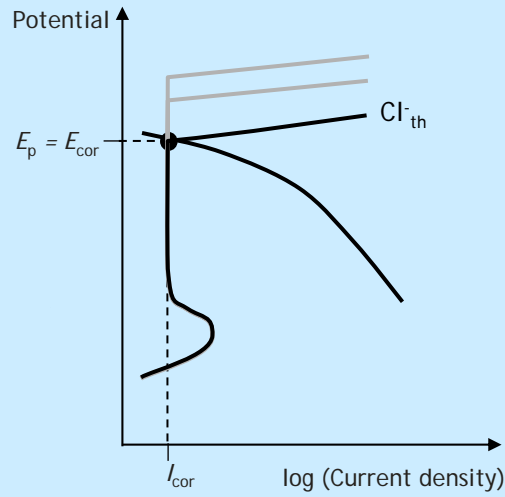






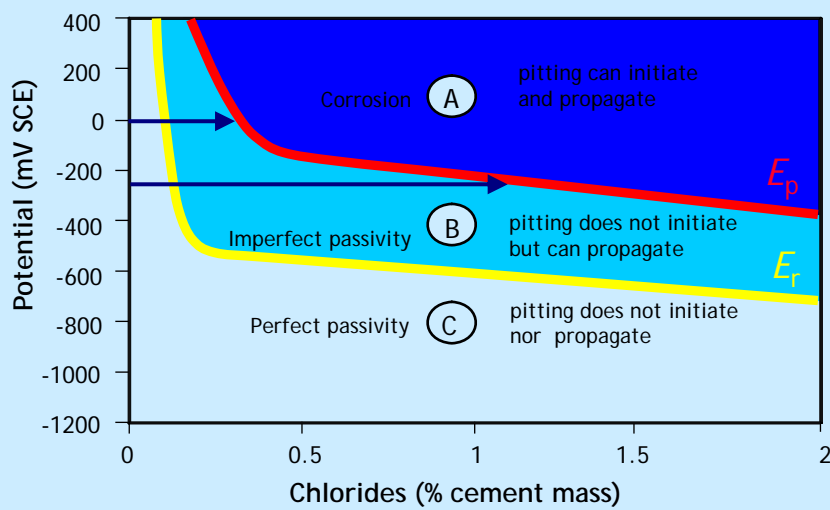
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## Electrochemical behaviour of steel in concrete

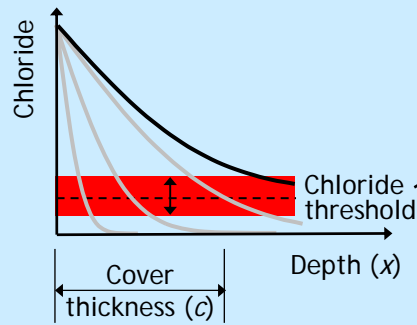
L. Bertolini - Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



P. Pedefferri, L'Edilizia, 1992 / Constr. Build. Mat., 10, 1996



## Chloride induced corrosion



- 1) potential (moisture content)
- 2) type of binder (pH of pore solution, binding, ...)
- 3) voids at the steel-concrete interface
- 4) temperature
- 5) steel composition and surface finishing
- 6) ...



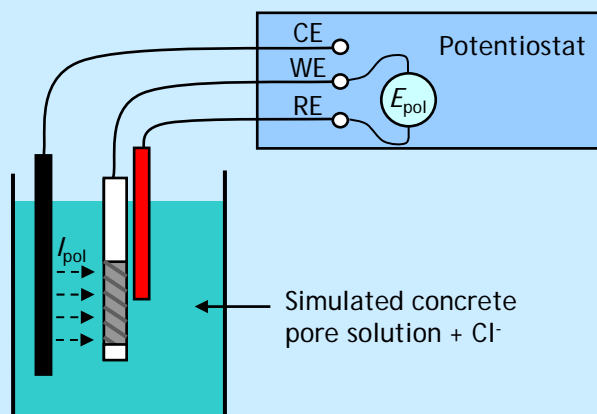
Concrete



L. Bertolini. Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



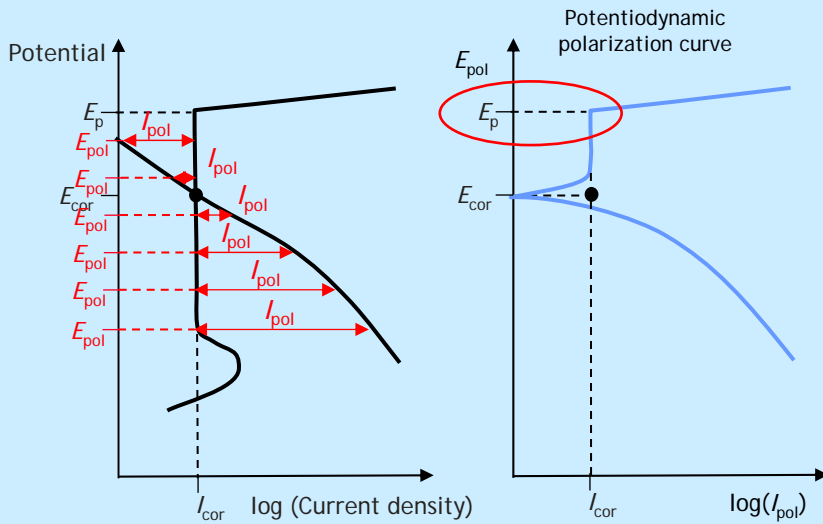
## Electrochemical tests in solutions



L. Bertolini. Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



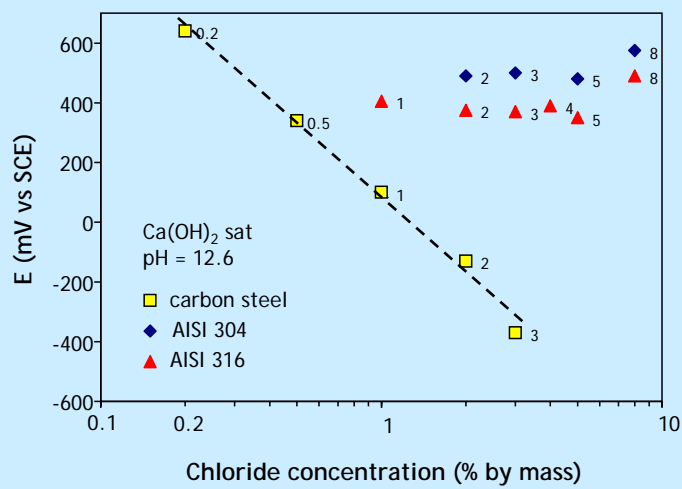
## Potentiodynamic polarization tests



L. Bertolini. Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Potentiodynamic polarization tests

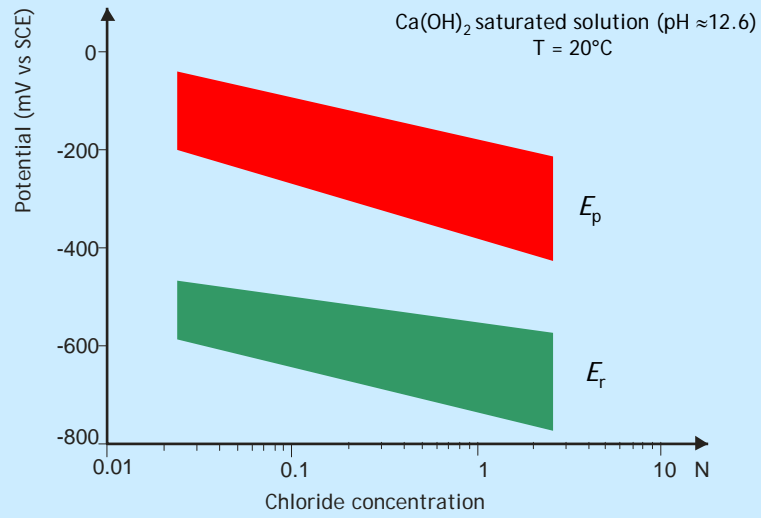


L. Bertolini. Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies

L. Bertolini *et al.*, Brit. Cor. Journ., 31, 3, 1996



## Potentiodynamic polarization tests

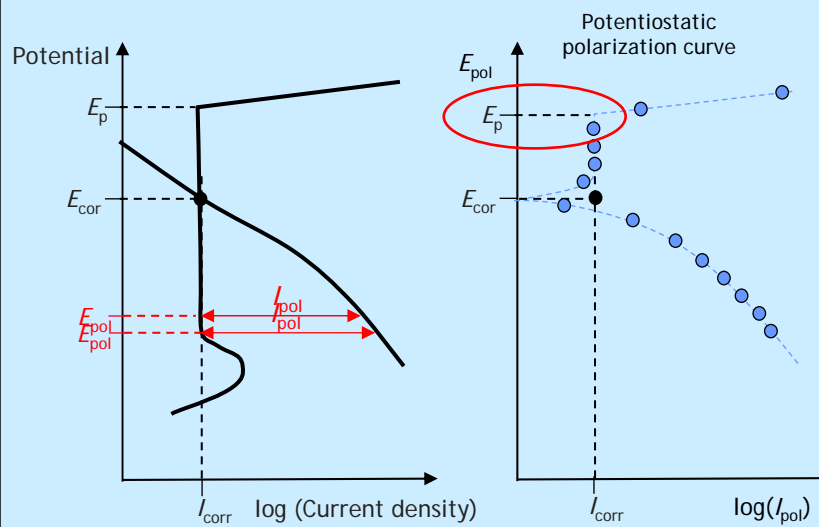


L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies

R. Cigna, O. Fumei, L'industria italiana del cemento, 9, 1981



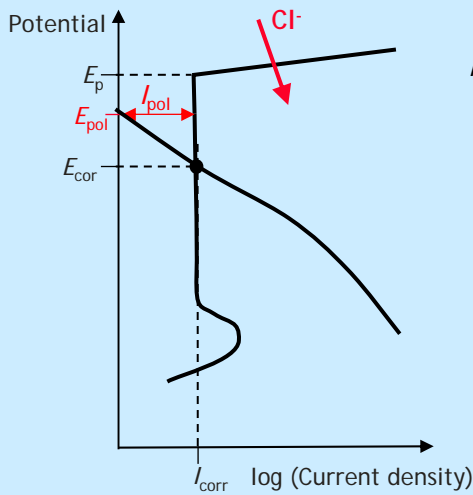
## Potentiostatic polarization tests



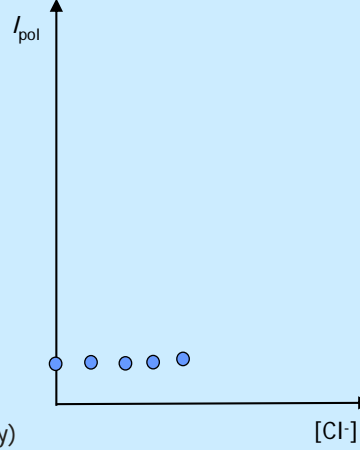
L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Potentiostatic polarization tests



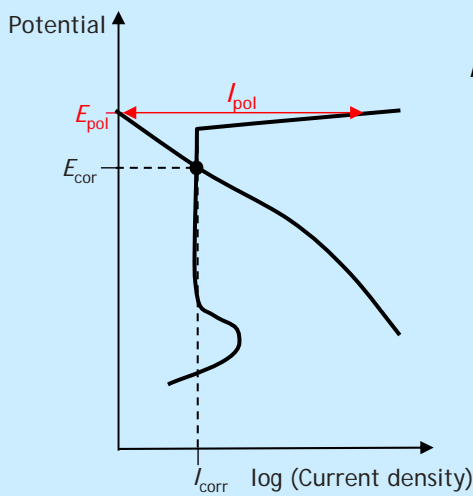
Potentiostatic polarization tests  
(Constant potential / added chloride)



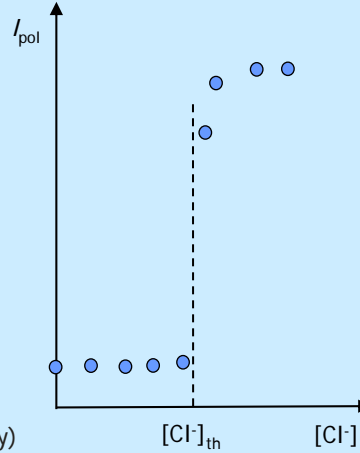
L. Bertolini - Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Electrochemical behaviour of steel in concrete



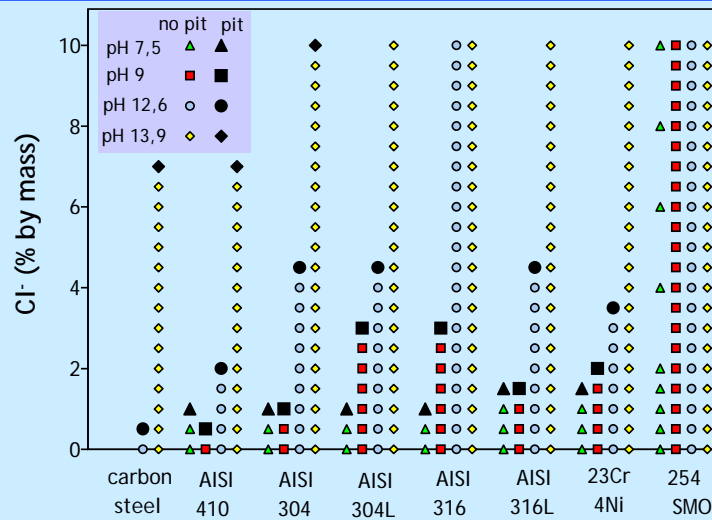
Potentiostatic polarization tests  
(Constant potential / added chloride)



L. Bertolini - Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Potentiostatic polarization tests



Imposed potential: +200 mV vs SCE  
Chloride added at intervals of 48 h

L. Bertolini *et al.*, Brit. Cor. Journ., 31, 3, 1996

L. Bertolini. Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Limitations of solution tests

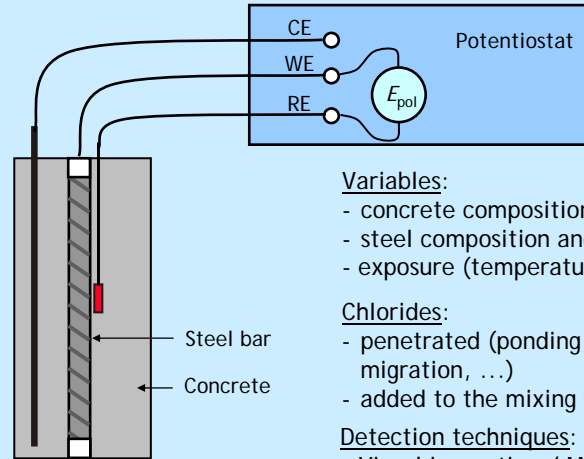
- composition of the testing solution
- steel/solution interface vs steel/concrete interface
- chloride content (% mass in solution vs % mass cement)
- time of polarization / scan rate
- ...

L. Bertolini. Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Tests in concrete (or mortar)

L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



### Variables:

- concrete composition and properties
- steel composition and properties
- exposure (temperature, humidity, etc.)

### Chlorides:

- penetrated (ponding, wet/dry cycles, migration, ...)
- added to the mixing water

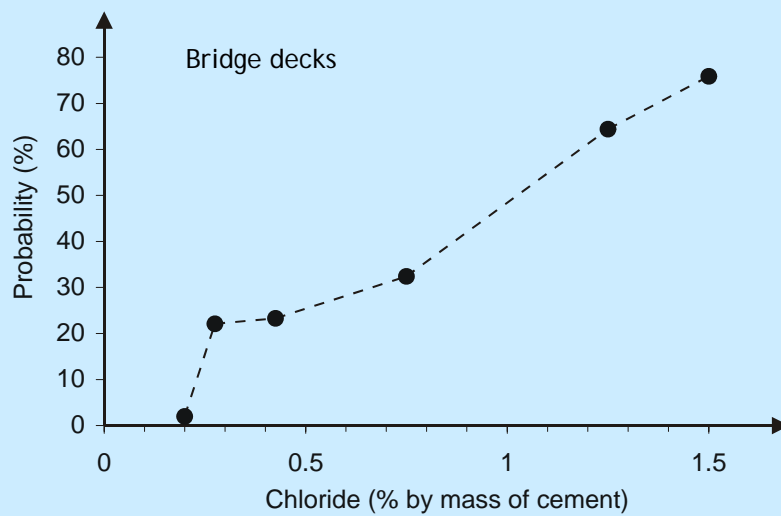
### Detection techniques:

- Visual inspection / Mass loss
- Free corrosion conditions ( $E_{cor}$ ,  $I_{cor}$ )
- Polarization tests
- Macrocell tests ( $\Delta E$ ,  $I$ )



## Visual inspection / mass loss

L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies

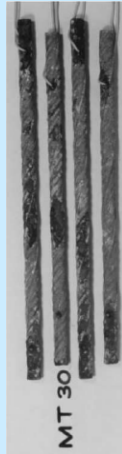


P. R. Vassie, Proc. of Inst. Of Civ. Eng., 1984

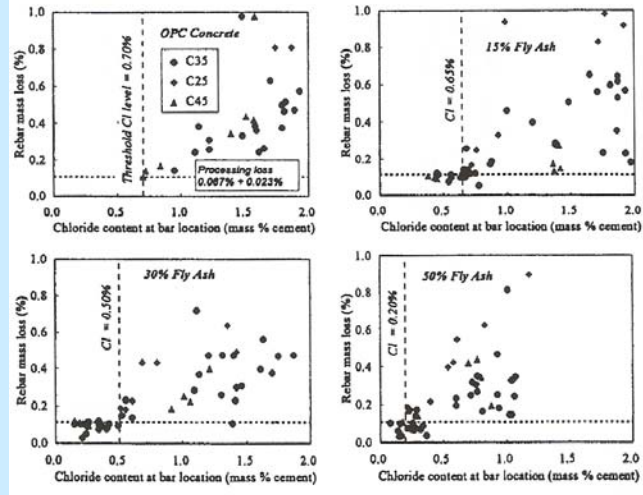


## Visual inspection / mass loss

Marine exposure  
(tidal zone)  
4 years



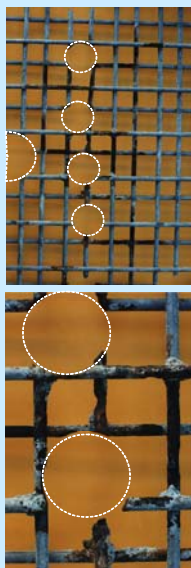
L. Bertolini. Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



M. Thomas, Cement and Concrete Research, 26, 1996



## Visual inspection / mass loss



5 years ponding with 3.5% NaCl

Cathodic current density (mA/m <sup>2</sup> )	Corroded area (%)	Maximum depth of attack (mm)	E (mV) vs Ti/MMO*	Cl <sup>-</sup> vs cement content (%)
Control	2.5	1.5	-400 / -500	1.5
0.4	0.7	1	-400 / -500	1.7
0.8	0.7	0.8	-500 / -600	2
1.7	0	0	-600 / -700	2.5
4.2	0	0	-700 / -900	3.5

L. Bertolini. Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies

L. Bertolini *et al.*, COST 521 Final Workshop, 2002

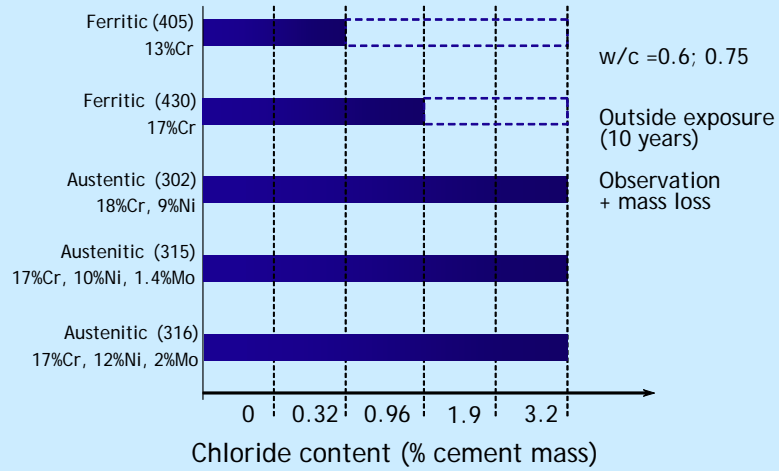




## Visual inspection / mass loss

Stainless steel bars

Mixed-in chloride



K. W. Treadaway *et al.*, Proc. of Inst. Of Civ. Eng., 1989

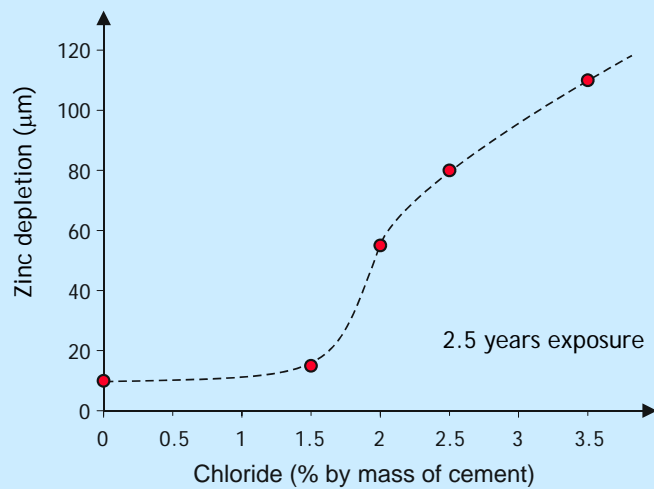
L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Visual inspection / mass loss

Galvanized steel bars

Mixed-in chloride

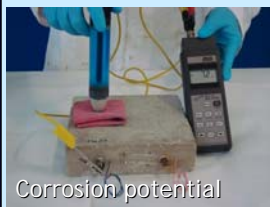


U. Nuernberger, W. Buel, Materials and Corrosion, 42, 1995

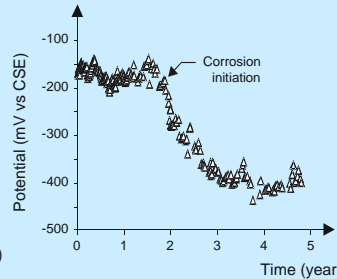
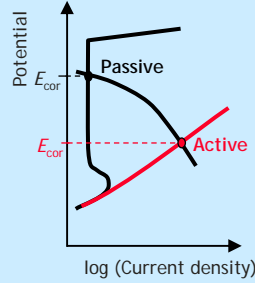
L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



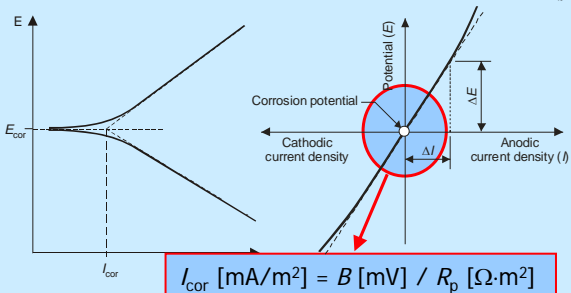
## Monitoring corrosion potential and corrosion rate



Corrosion potential



Corrosion rate

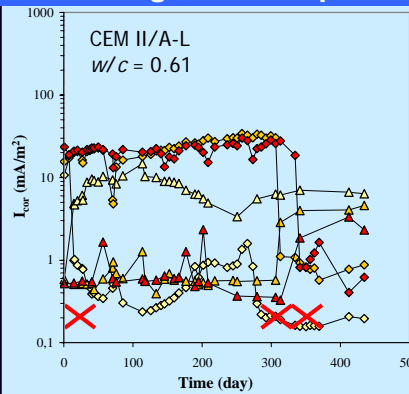


$$I_{cor} [\text{mA/m}^2] = B [\text{mV}] / R_p [\Omega\text{-m}^2]$$

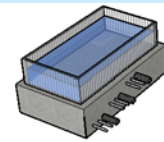
L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



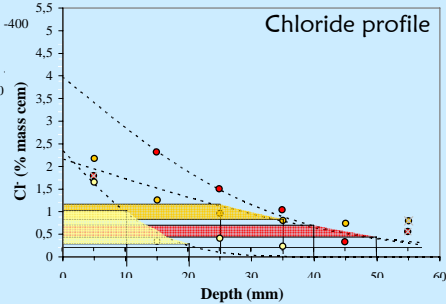
## Monitoring corrosion potential and corrosion rate



Penetrated chlorides (ponding)



"Depassivation":  
 $E_{cor} < -350 \text{ mV vs SCE}$   
 $I_{cor} > 2.5 \text{ mA/m}^2$

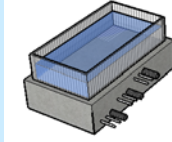
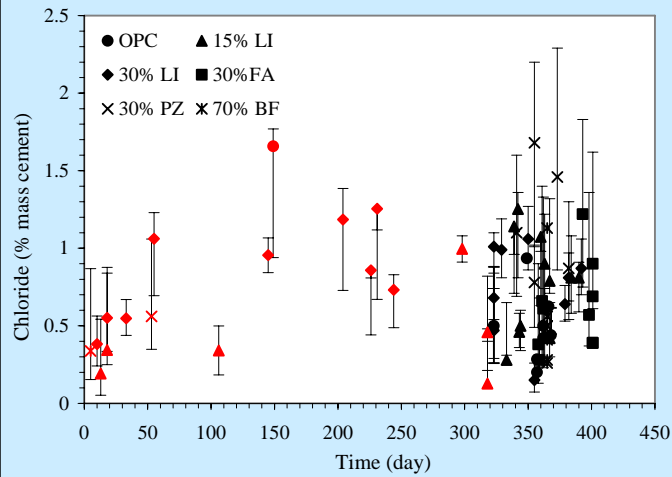


F. Lollini, PhD Thesis, Politecnico di Milano, 2008

L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Monitoring corrosion potential and corrosion rate



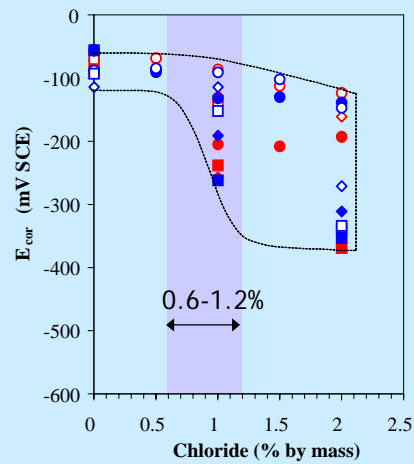
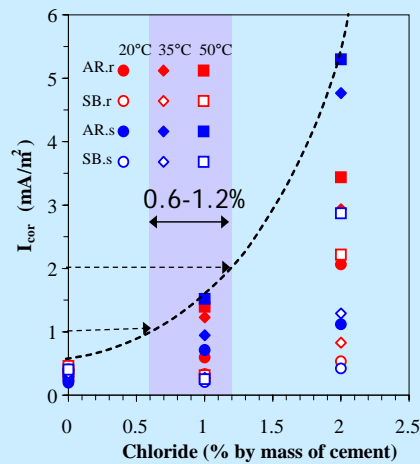
L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies

F. Lollini, PhD Thesis, Politecnico di Milano, 2008



## Monitoring corrosion potential and corrosion rate

10%SF concrete - Mixed-in chloride



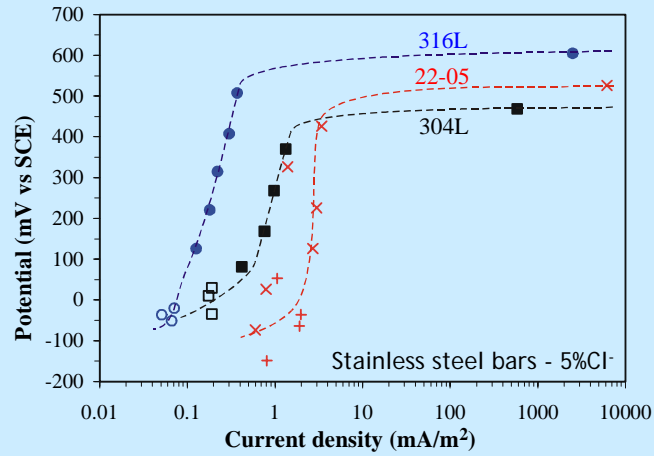
L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies

M. Manera *et al.*, Corrosion Science, 50, 2008



## Potentiostatic polarization tests

Potential steps (constant Cl<sup>-</sup>)

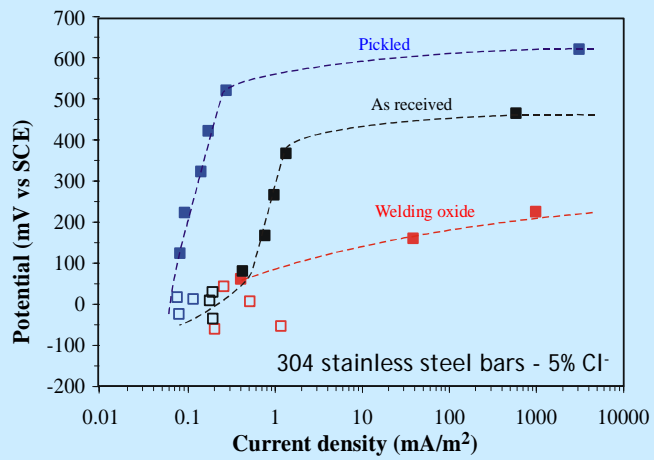


L. Bertolini *et al.*, 15th ICC, Granada, 2002



## Potentiostatic polarization tests

Potential steps (constant Cl<sup>-</sup>)

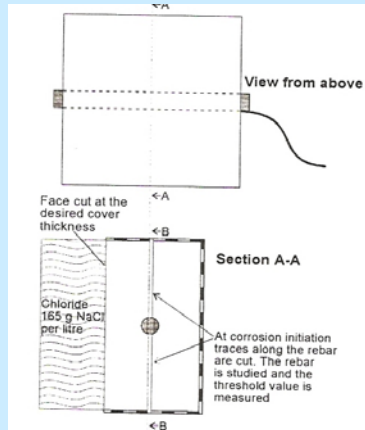


L. Bertolini *et al.*, 15th ICC, Granada, 2002

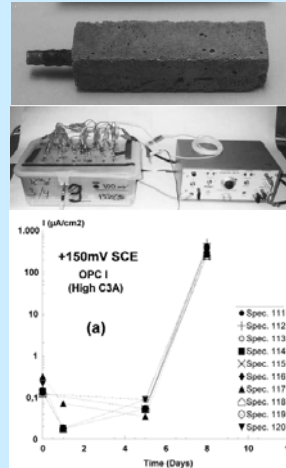


## Potentiostatic polarization tests

Constant potential (penetrating chloride)



J. M. Frederiksen, Rilem Workshop, 2000



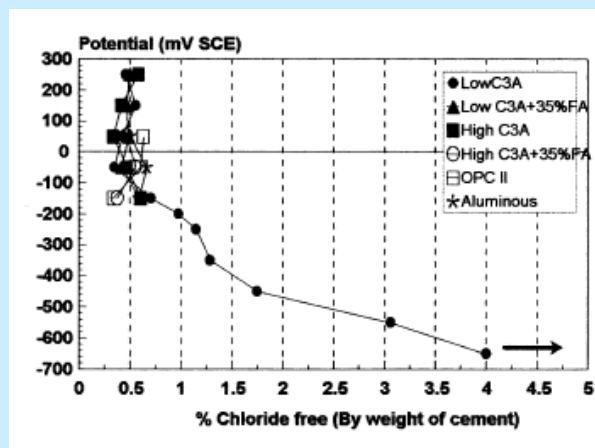
M. C. Alonso *et al.*, Rilem Workshop, 2000



## Potentiostatic polarization tests

Constant potential (penetrating chloride)

Mortar  
 $w/c = 0.5$   
 7 day curing  
 6 mm ribbed bar  
 cover = 5 mm

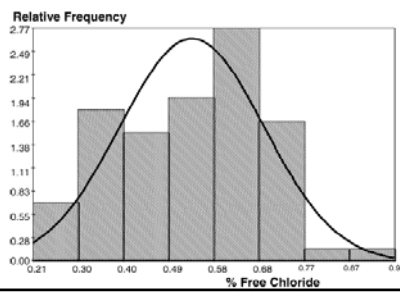
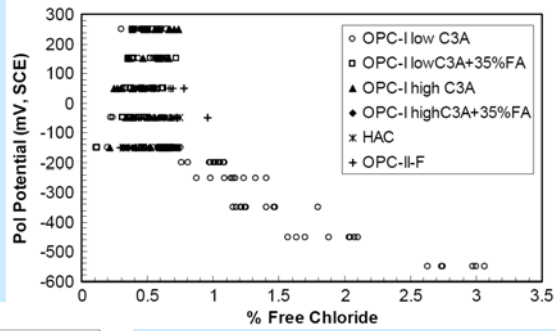


M. C. Alonso *et al.*, Electrochimica Acta, 47, 2002



## Potentiostatic polarization tests

Mortar  
 $w/c = 0.5$   
7 day curing  
6 mm ribbed bar

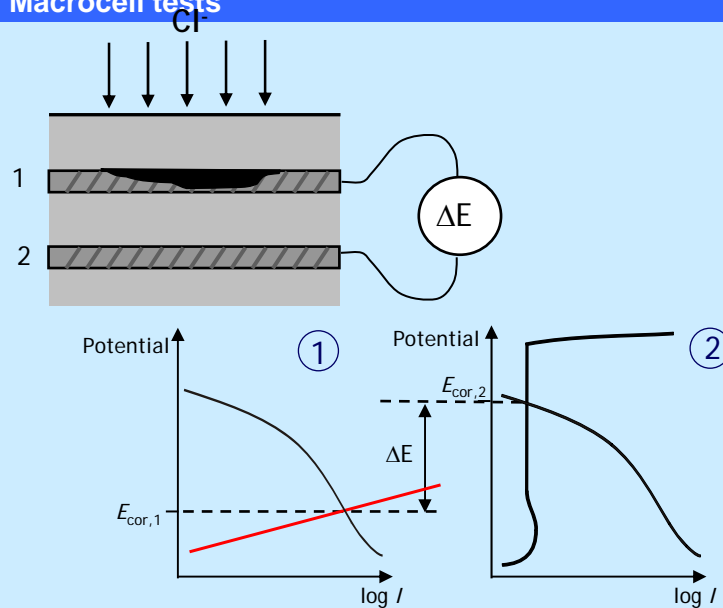


D. Izquierdo *et al.*, *Electrochimica Acta*, 49, 2004

L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Macrocell tests

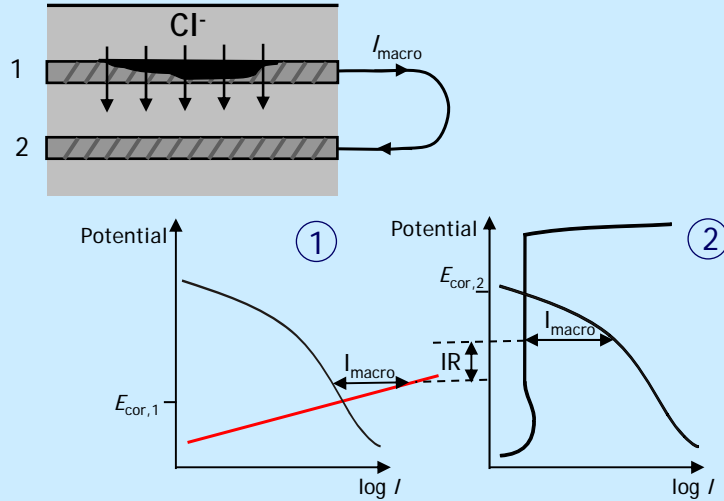


L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



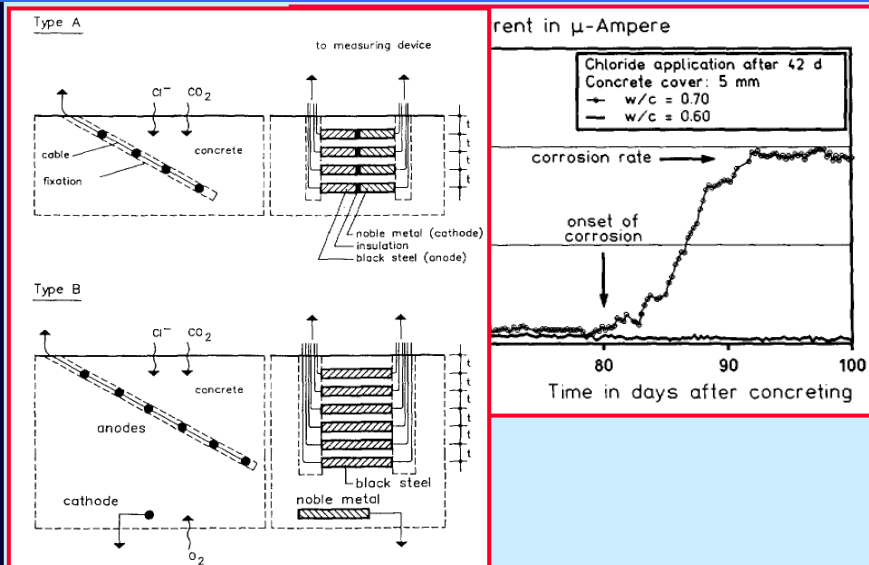
## Macrocell tests

L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



## Macrocell tests

L. Bertolini, Depassivation of steel in case of pitting corrosion  
Detection techniques for laboratory studies



M. Raupach, P. Schiessl, Const. Build. Mat., 11, 1997



## Concluding remarks

Different techniques have been utilized for the detection of "corrosion initiation" or "depassivation" of steel during laboratory tests, depending on the type of test adopted for the study of the chloride threshold.

Solution tests → Polarization tests ( $E_{\text{pit}}$  vs  $Cl$  or  $Cl_{\text{th}}$  vs  $E_{\text{pol}}$ )

Tests in concrete → Mass loss / Visual observation

→  $E_{\text{cor}}$ ,  $I_{\text{corr}}$

→ Potentiostatic polarization tests

→ Macrocell tests

Different techniques focus on specific aspects of the "depassivation" process.

The methodology as well as the criterion defined for detecting corrosion initiation/depassivation may have a significant influence on the evaluation of the chloride threshold.





## **4 Chloride threshold values in the literature**

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### **“Chloride threshold values in the literature”**

*Maria Cruz Alonso*

*Institute of Construction Science Eduardo Torroja*



## CHLORIDE THRESHOLD VALUES IN THE LITERATURE

M Cruz Alonso

Institute of Construction Science Eduardo Torroja (IETcc-CSIC)

Madrid (Spain)

([mcalonso@ietcc.csic.es](mailto:mcalonso@ietcc.csic.es))

Penetration of chloride ions from de-icing salts or marine environments are common causes for degradation of concrete structures and responsible for most of the damages and investment in repair works. By these reasons efforts are being devoted in standards and construction codes in order to give rules and guidelines for designing durable structures. Also efforts are being derived to the developing of models, deterministic or probabilistic, to more accurately approaches for the calculation of the service life of concrete structures, although most of them are based on Tuutti's Model.

Service life models consider that reinforced concrete exposed to chloride polluted environments initiate corrosion when a certain amount of chlorides arrives to the rebar surface. The so-called chloride threshold level is considered an essential parameter for assessing the probability of reinforcement corrosion, and becomes one of the key parameters needed for service life prediction, being of interest to have tests methods and expressions to introduce in the models. The specific conditions that allow the chlorides to reach the threshold for corrosion initiation are still not established, which prevents the use of a representative value in the calculation of service life of concrete structures.

In spite of the numerous studies performed to establish the critical chloride level for the onset of corrosion, a wide range of chloride threshold values have been suggested even using apparently similar testing conditions and materials, which makes not feasible to define a single value. Thus, a reliable quantification of the critical chloride content is considered a prerequisite for service life calculation. The reason has been attributed to the number of variables that affect the chloride threshold, among them are: the type and content of cement, the exposure conditions, the distance from the sea in marine environments, the time of exposure, the environmental temperature, the oxygen availability at the rebar surface, the type of steel, the electrical potential of the rebar surface, presence of cracks etc. Other reasons exist for a non unique chloride threshold value, derived from the methodology employed to detect depassivation and the parameter to express the threshold. From this analysis it can be concluded that, at present, a significant lack of critical analyses on the chloride threshold is observed resulting in a large uncertainty in the values used for reinforcement corrosion onset. It is therefore a great practical importance to reduce this uncertainty based on a common approach supported by appropriate experimental investigations.

One general aspect still not fully agreed, that also contribute for no founding a unique chloride threshold value, is the form to express the threshold, in percentage of total or free chloride by weight of binder in concrete, or as  $[Cl^-]/[OH^-]$  ratio. Although  $[Cl^-]/[OH^-]$  seems to be the most accurate expression, as include not only the critical chloride but also informs on the ability of the concrete to passivate the reinforcement and inhibit corrosion onset. However due to the difficulty in measuring  $[OH^-]$  in concrete, the free and total chloride contents have been more widely used, in particular construction codes refer to total chloride. Besides the free %Cl and the  $[Cl^-]/[OH^-]$  expressions show widest scatter of threshold values in literature.

Most of the authors for prediction of critical chloride concentration for depassivation of reinforcements have used stochastic models, nevertheless values defined in standards have usually

been adopted; however in many cases these values are very conservative. To make a more sense approach, statistical analysis has been used. Hausman in the sixties was the first that gave an statistical threshold distribution to predict rebar depassivation, using a  $[Cl^-]/[OH^-]$  ratio and giving a mean value of 0.6 but with a wide variation coefficient of 30%. Since then other authors have tried to make statistical approaches, proposing uniform distributions of chloride for critical concentrations giving mean values of 0.25 % of total chloride by weight of cement with a variation coefficient of 19 %, or 0.5 % with variation coefficient of 36 %, also fittings for a log normal distribution have been made giving values, with 95% provability for reinforcement depassivation, from 0.496% to 0.569% for free chlorides and from 0.623% to 0.771% for total chlorides, with a minimum value for 5% depassivation risk of 0.280% for free chlorides and 0.316% for total chlorides. Finally in a recent fitting made by present author using all chloride threshold values reported in the literature have allowed to define histograms as those of figures 1 and 2 for free and total chlorides.

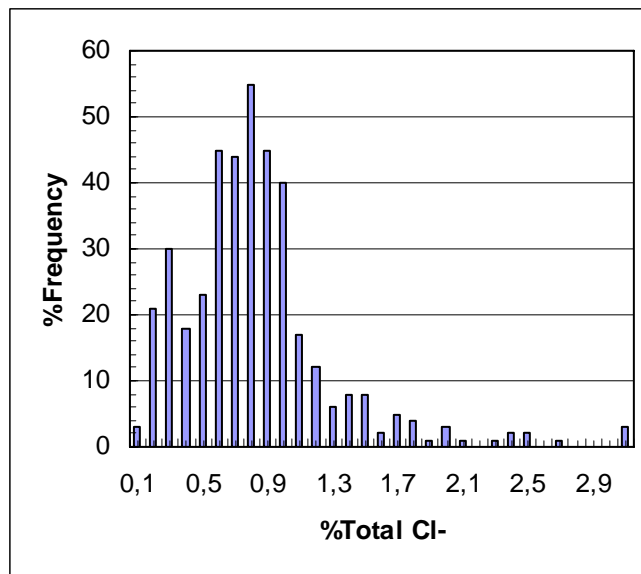


Figure 1. Histogram of the total chloride threshold from the values published.

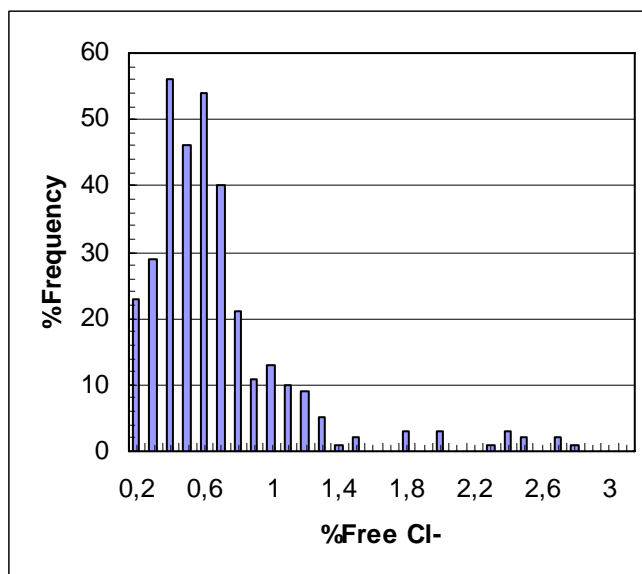


Figure 1. Histogram of the free chloride threshold from the values published.

## 5 Chloride sensors in concrete

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### **“Chloride sensors in concrete - Accuracy, long-term stability and application”**

*Bernhard Elsener*

*ETH Zürich and University Cagliari*



COIN Workshop  
on Critical Chloride Content in Reinforced Concrete  
Trondheim 5./6. June 2008



**Chloride Sensors in Concrete -**  
Accuracy, Long-term Stability, Application

Bernhard Elsener  
ETH Zürich and University Cagliari  
elsener@ethz.ch



## Condition assessment

- Visual Inspection
- Half-cell potential mapping
- Concrete resistivity
- Corrosion rate

## Monitoring

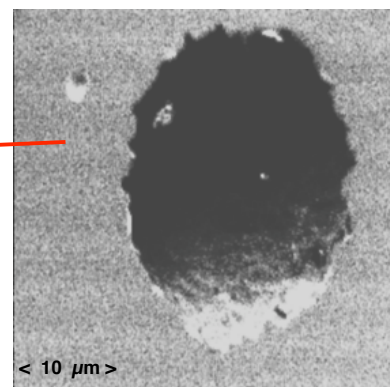
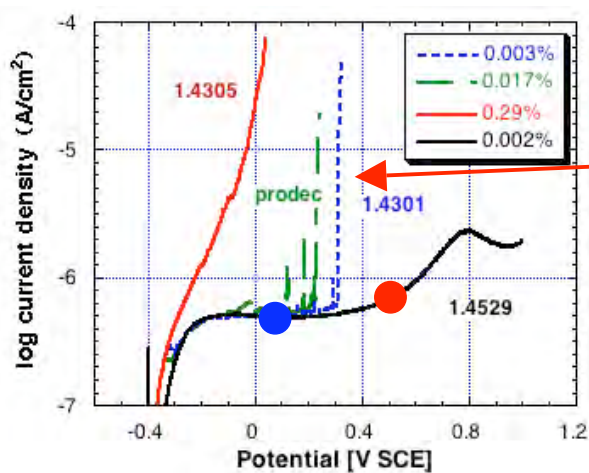
- Potential of the reinforcement
- Concrete resistance
- Polarization resistance
- Chloride sensors
- pH sensors



Direct information on “critical chloride content” only with sensors

# Critical chloride content

Determine pitting potential is only half of the truth....



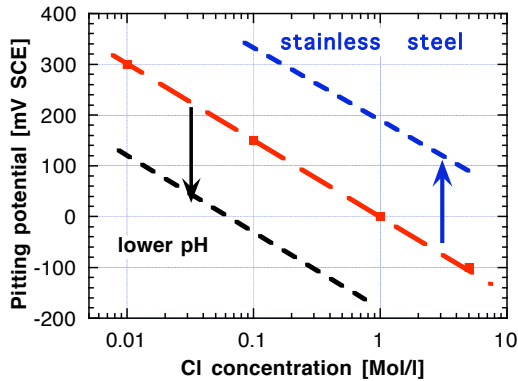
In practical situation - what parameters determine if the potential is **above** or **below** the pitting potential ?

# Critical chloride content

Condition for depassivation  $E_{\text{corr}} > E_{\text{pit}}$

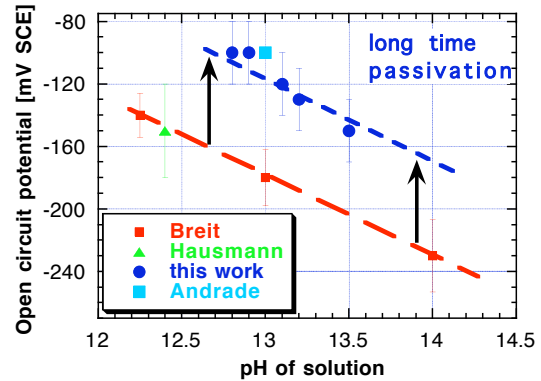
## Pitting potential $E_{\text{pit}}$

Chloride content (**free Cl<sup>-</sup>**)  
Reinforcement material, ...



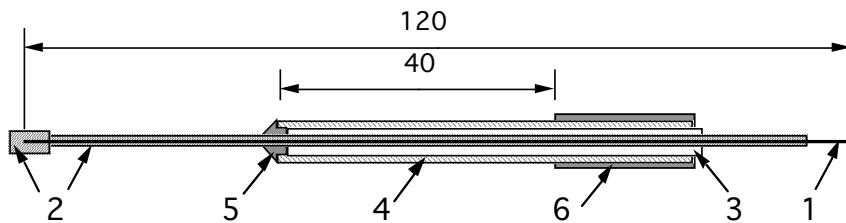
## Corrosion potential $E_{\text{corr}}$

pH of pore solution  
Oxygen availability, ...



# Chloride sensor

Combined chloride and resistivity sensor element.



1 silver wire, 2 AgCl coating, 3 teflon tube (isolation),  
4 stainless steel tube (1.4301), 5 epoxy sealing, 6 insulation.  
Total length ca. 12 cm

B. Elsener et al., Proc. RILEM Int. Workshop, ed. L.O. Nilsson, RILEM (1997) p. 17 - 26  
B. Elsener et al., Materials and Corrosion 54 (2003) 440 - 446

Chain  $\text{Ag} / \text{AgCl} // a_{\text{Cl}^-} / \text{KCl} // \text{Hg}_2\text{Cl}_2 / \text{Ag}$

Nernst Law

$$E (\text{AgCl}/\text{Cl}^-) = E_o + RT/nF * \ln ([\text{Cl}^-] / [\text{AgCl}])$$

$$E (\text{AgCl}/\text{Cl}^-) = E_o + 0.059 * \log ([\text{Cl}^-])$$

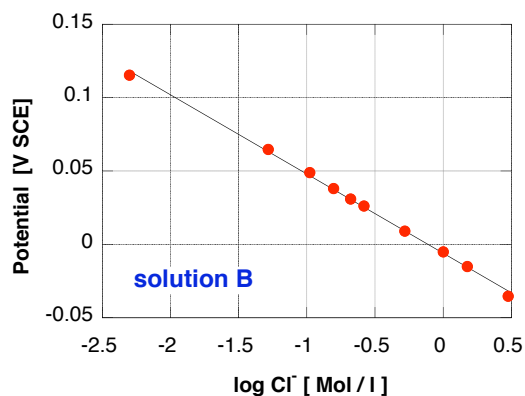
Calibration curves

## Further questions

- Activity coefficients
- Stability of reference electrode
- Stability of chloride sensor
- Junction potentials

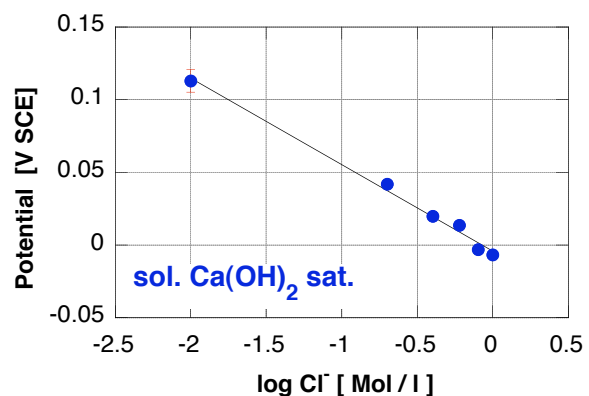
# Calibration curves

Synthetic pore solution (pH 13.5)



$$y = - 6.5 \pm 1.4 - 54.4 \pm 1.3 * \log x$$

Ca(OH)<sub>2</sub> solution sat. (pH 12.5)



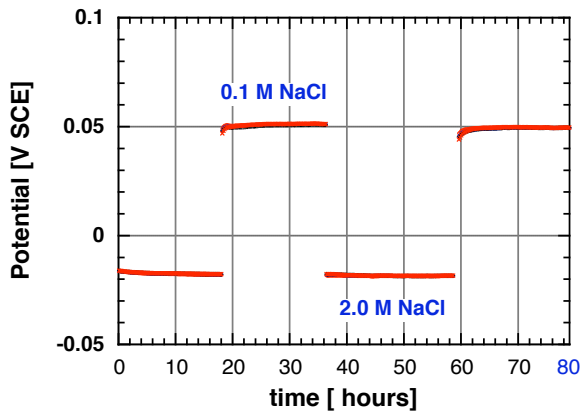
$$y = - 4.3 \pm 1.2 - 59.4 \pm 1.1 * \log x$$

Similar values of the slope were reported for other solutions

B. Elsener et al., Proc. RILEM Int. Workshop, ed. L.O. Nilsson, RILEM (1997) p. 17 - 26  
 L. Zimmermann, PhD Thesis No. 13870 ETHZ (2000)

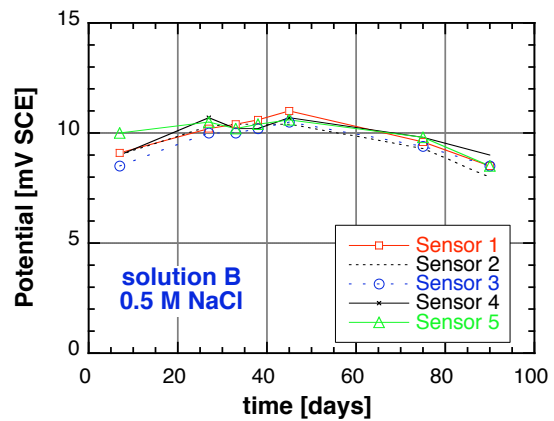
# Long term stability

Cyclic concentration change (5 sensors)



Standard deviation < 2 mV

Long term stability (solution)

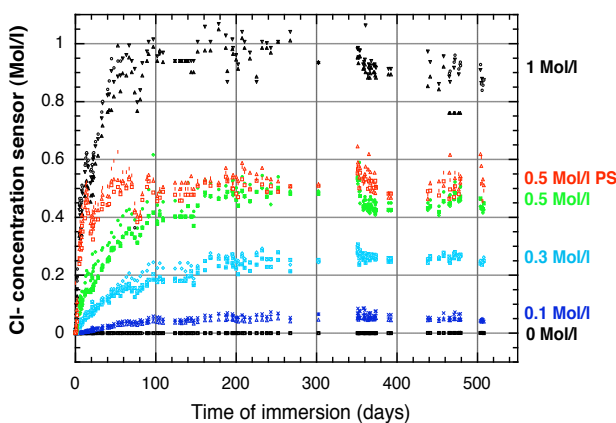


Standard deviation < 2 mV  
Very low drift (no T correction)

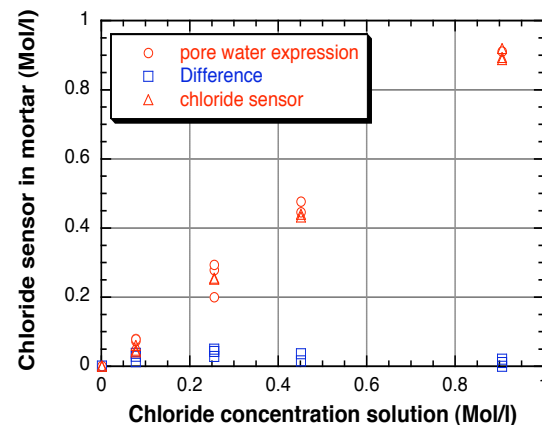
B. Elsener et al., Proc. RILEM Int. Workshop, ed. L.O. Nilsson, RILEM (1997) p. 17 - 26  
L. Zimmermann, PhD Thesis No. 13870 ETHZ (2000)

# Experiments in mortar

Small cylindrical mortar samples (ø 4 cm, height 4 cm, w/c 0.5, 500 d)



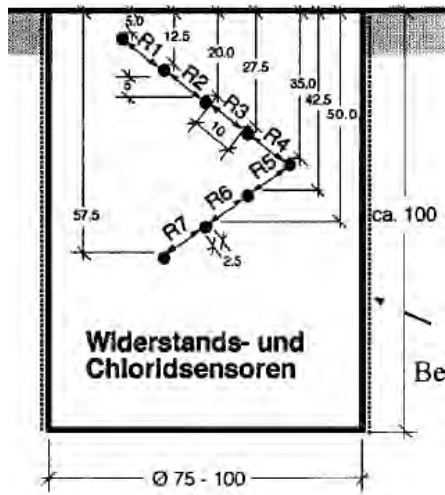
Follow chloride uptake into samples



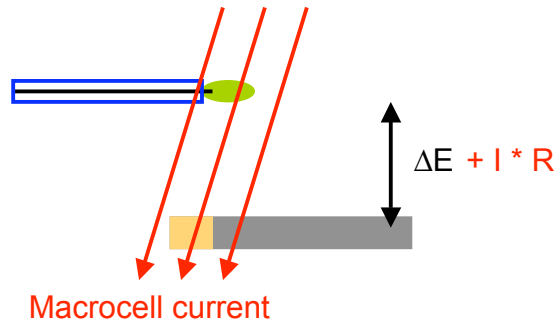
Good agreement between sensors and pore water expression, but...

L. Zimmermann, PhD Thesis No. 13870 ETHZ (2000) - Final report COST 509

## Instrumented cores



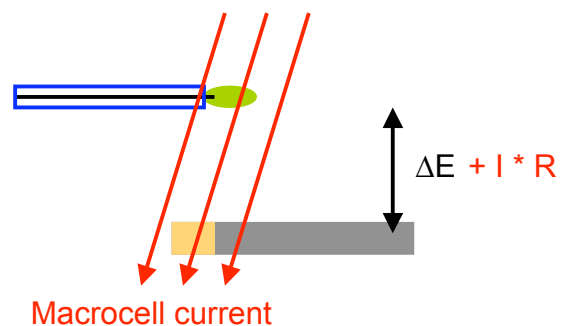
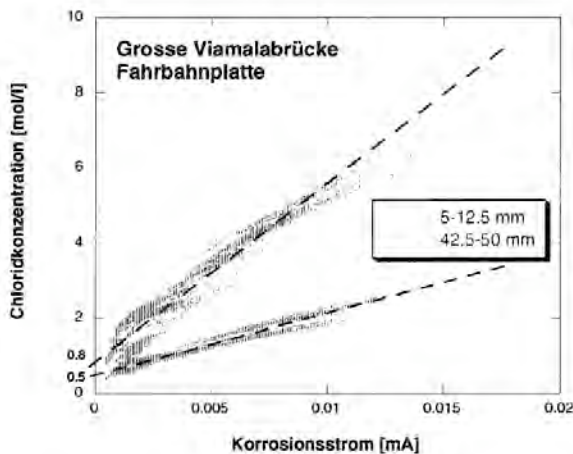
Work well in the laboratory. When mounted on structures, additional problem:



Potential difference between sensor and reference electrode is affected by macro-cell current -> wrong chloride content

Y. Schiegg, PhD Thesis No. 14583 ETHZ (2002)

## Influence of macrocell current



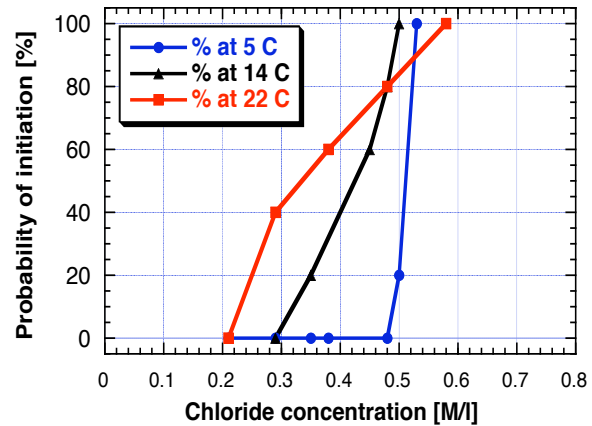
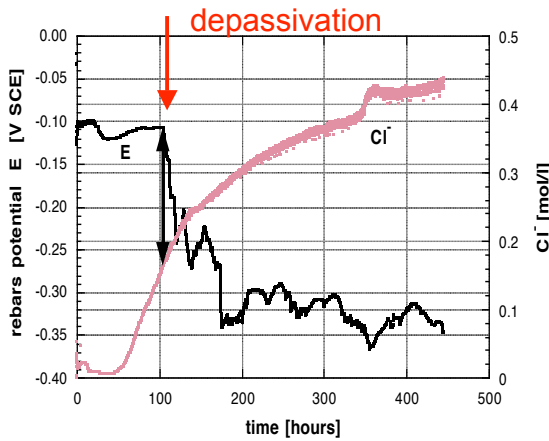
Potential difference between sensor and reference electrode is affected by macro-cell current -> wrong chloride content. Application limited.

Y. Schiegg, PhD Thesis No. 14583 ETHZ (2002)

# Pitting initiation

Can be detected by drop in potential

...is a stochastic process



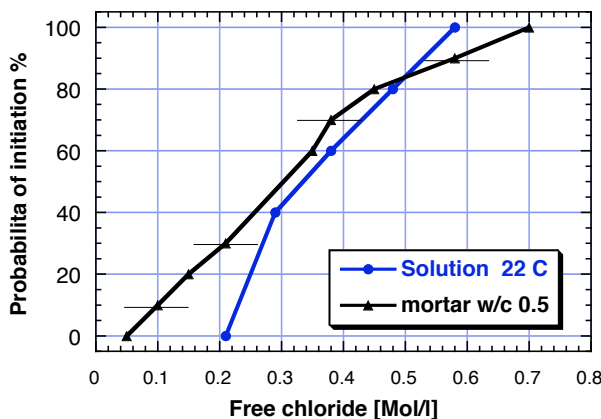
Time of depavassation can be detected  
Free chloride content measured

Critical chloride content is distributed,  
mean value and standard deviation.

L. Zimmermann, PhD Thesis No. 13870 ETHZ (2000), B. Elsener et al., EUROCORR '98

# Pitting initiation

Comparison mortar / solution



Pit initiation (depavassation) in  
mortar is more distributed

More variables to control:

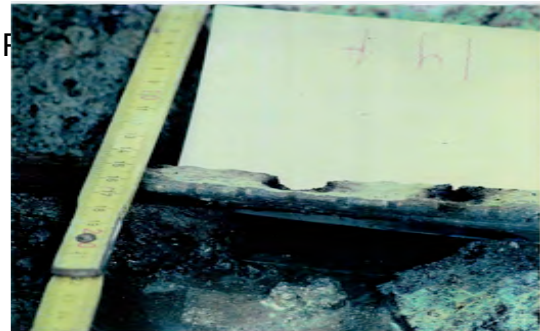
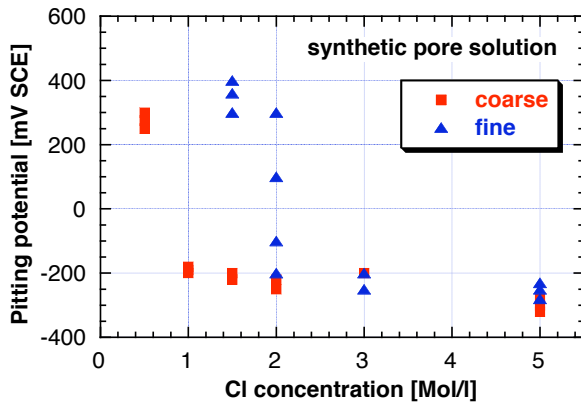
- age of sample
- cover depth (oxygen availability)
- corrosion potential

In agreement with practical  
experience - critical chloride  
content is not a constant.

Pore solution, OH<sup>-</sup> conc. 0.64 Mol/l  
Mortar w/c 0.5, ca. 0.5 Mol/l

L. Zimmermann, PhD Thesis No. 13870 ETHZ (2000), B. Elsener et al., EUROCORR '98

Influence of surface quality on  $E_{pit}$

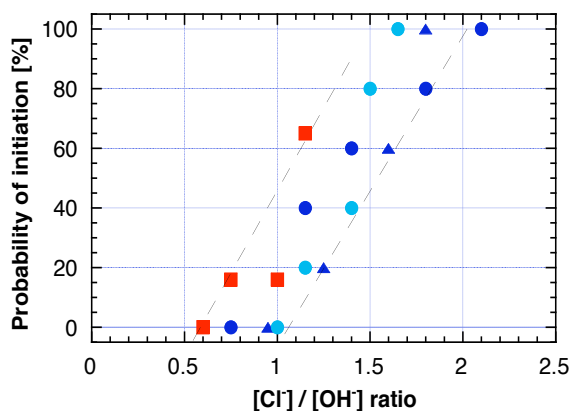


Rough surface shows lower pitting potential

Pit propagation - other controlling factors

L. Zimmermann, PhD Thesis No. 13870 ETHZ (2000), B. Elsener et al., EUROCORR '98

# Cl<sup>-</sup>/OH<sup>-</sup> ratio



■ According to Hausmann (1967)

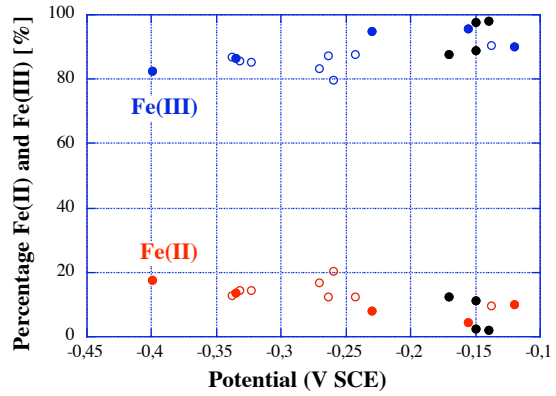
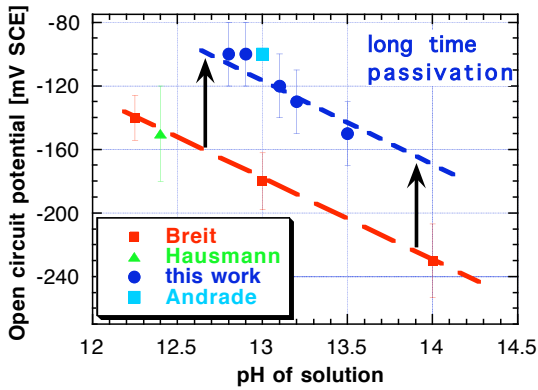
● Pore solution, pH 13.2 - 13.5

Stochastic feature of pit initiation and distribution remains valid

Several works of different authors can be "normalized"

Most important is not the value of the Cl<sup>-</sup>/OH<sup>-</sup> ratio but its probabilistic distribution. This has to be taken into account for modeling and service life prediction

# Corrosion potential



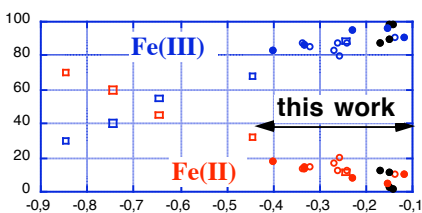
For passive steel in concrete  $E_{corr}$  is a function of pH and time

Increasing potential leads to a passive film rich in Fe(III) - more protective

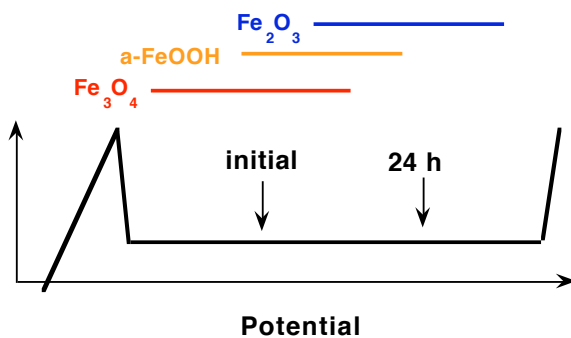
- The passive film on the reinforcement shows “ageing” phenomena
- Protective properties improve with time of exposure to alkaline environment

A. Rossi, B. Elsener, EUROCORR 2001

# Passive film composition



Electrochemical potential of steel in alkaline solutions is related to (controlled by ?) surface composition



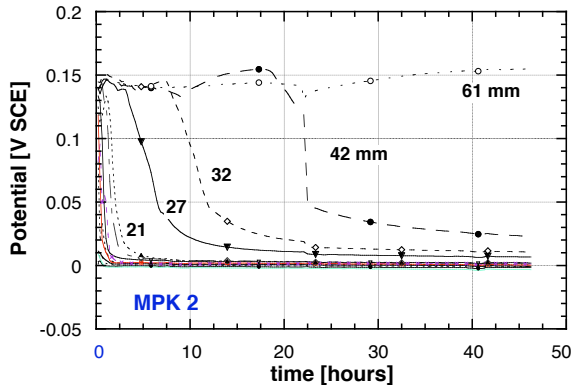
Presence of different oxide phases on steel in 0.1 M NaOH solution

A. Rossi, B. Elsener, EUROCORR 2001



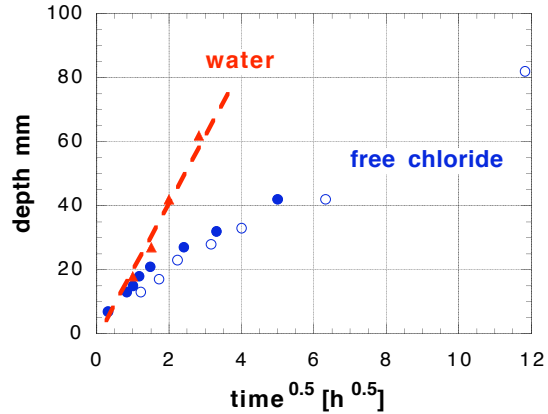
# Chloride ingress

Instrumented mortar blocks with chloride sensors at different depths



Drop in potential indicates increase in chloride concentration

Comparison of water uptake (resistance) and chloride ingress

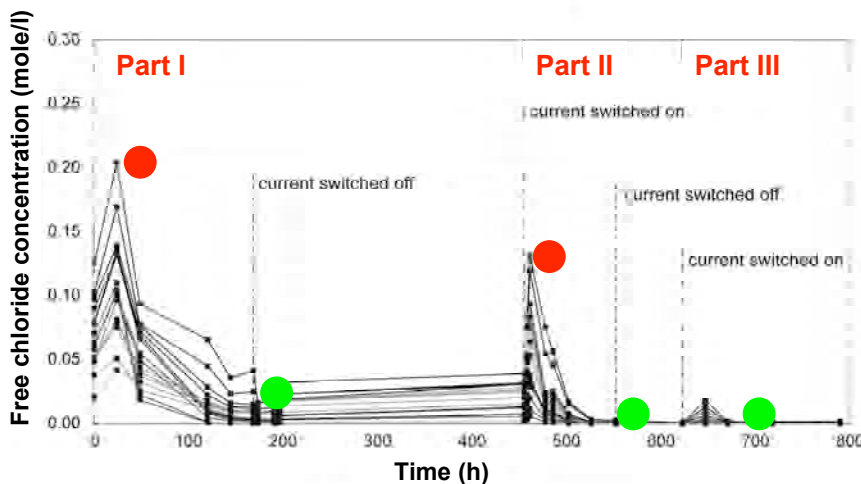


Water ingress follows  $\sqrt{t}$  law. Chloride ingress slowed down by binding

B. Elsener et al., Proc. RILEM Int. Workshop, ed. L.O. Nilsson, RILEM (1997) p. 17 - 26

# Control of ECE

Electrochemical chloride removal controlled by sensors



Free Cl<sup>-</sup> content measured with chloride sensors "in-situ"

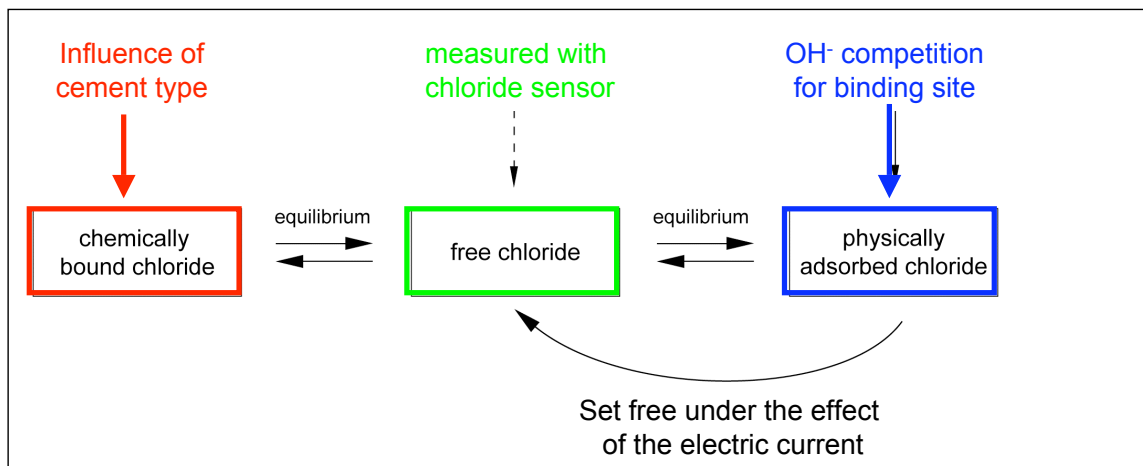
Mortar, w/c 0.5  
Chloride ingress by capillary suction

Current 1 A/m<sup>2</sup> steel

- free chloride concentration decreases rapidly within few days
- After current switch off an increase in free Cl is found

U. Angst, B. Elsener, Corrosion Science (2008)

## Proposed types of chloride binding in chloride



- Equilibrium between chemically bound and free chloride
- but also between adsorbed and free chloride - effect of current

U. Angst, B. Elsener, Corrosion Science (2008)

## Summary

- The chloride sensitive AgCl element measures the free chloride content in solutions and in porous materials like mortar or concrete
- The measurement requires a stable reference electrode
- The measured potential (especially with surface RE) may be affected by liquid junction potentials, membrane potentials etc. This will decrease the accuracy of the sensor
- The combined chloride / resistance sensor has numerous applications in research in laboratory as has been shown in this presentation
- Field applications are difficult due to macro-cell currents

The critical chloride content is an important design-parameter for service life

- It is not a constant but distributed due to the probabilistic nature of pitting corrosion
- Defined as **free chloride** content that leads to depassivation of the steel
- Influenced by a number of parameters



For service life prediction

- Take into account total chloride might be dissolved !
- Take into account pH, O<sub>2</sub> changes

I would not rely on the assumption of low corrosion rate...



Thank you for your attention -  
and your discussions

## **6 Laboratory experiments for detecting critical chloride content**

### **“Laboratory experiments for detecting critical chloride content in reinforced concrete”**

*Ueli Angst*

*NTNU, Norwegian University of Science and Technology*



# Laboratory experiments for detecting critical chloride content in reinforced concrete

UELI ANGST

NTNU Norwegian University of Science and Technology, Department of Structural Engineering  
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ueli.angst@ntnu.no

## Introduction

The knowledge of chloride threshold values for initiation of reinforcement corrosion in concrete is important for service life predictions and service life design. A lot of research has been devoted to finding such values. The reported results for critical chloride contents scatter over a wide range, e.g. from 0.02 to 3.08% when expressed in the form of total chloride by weight of binder [1]. This is mainly related to the variety of possible measurement techniques, both for field studies and laboratory setups. At present, no standardised or accepted testing method for critical chloride content exists.

A literature review over nearly 40 references reporting chloride threshold values has concluded that many studies were not practice-related [1]. Main pitfalls in laboratory work on critical chloride content have been identified to be the procedure to introduce chlorides and the quality of the steel-concrete interface. The latter is affected by both the rebar characteristics and the properties of the matrix. In many works, smooth rebars have been used instead of ribbed bars and the rebars have been prepared by sandblasting, polishing, cleaning, etc. Experiments have been conducted in alkaline solutions, or in cement paste, mortar or concrete. It is evident that the properties of the steel-concrete interface in the case of, for instance, smooth and polished rebars embedded in cement paste differ from reality. This difference is considered to be important since the steel-concrete interface has been identified to be one of the major influencing factors with regard to critical chloride content [2]. Also, compaction is usually better for laboratory concrete in comparison with real concrete. With regard to the chloride introduction, several techniques are available to accelerate chloride penetration in order to avoid time-consuming experiments as in the case of pure diffusion. However, the situation is different from reality, e.g. in the case of mixed-in chlorides where the steel might not be able to initially passivate.

The literature evaluation [1] also revealed that most critical chloride contents have been measured in terms of total chloride content by weight of binder; free chloride contents have primarily been reported in the case of experiments dealing with solutions or porous cement paste/mortar/concrete. This is mainly due to the limitations of the pore solution expression technique, which is usually the one used for obtaining samples for analysis of free chloride concentrations in concrete pore solution. Up to now, there is a lack of information on the critical chloride content in dense concrete (low w/c ratio, alternative cement types) on the basis of free chloride.

## Current project

The current project aims at measuring the critical chloride content based on both free and total chloride contents in laboratory concrete samples with a dense matrix. Emphasis is put on realistic and practice related conditions with regard to the factors mentioned in the previous section.

For the measurement of the free chloride content, embedded “chloride sensors” are used. These sensors consist of Ag/AgCl electrodes and have been used earlier by other researchers [3].

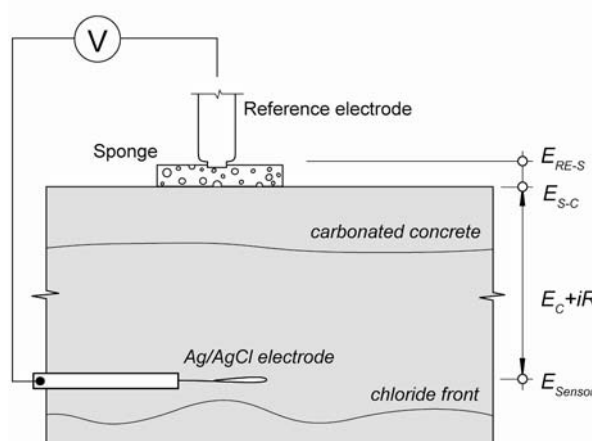
## Chloride sensors – direct potentiometry in concrete

The use of ion selective electrodes (ISE) in direct potentiometry is well established and has long been used in many fields such as analytical chemistry to determine the ionic activity of a certain species in aqueous solutions by a potential measurement. However, the situation in a cement based material such as concrete is more complicated. With regard to this, preliminary investigations have been undertaken by the present author. Some of the considerations and results are presented here; a more detailed description will follow in the full paper.

### *Sensitivity and error sources*

Potentiometric measurements are very sensitive to variations in potential. The sensitivity directly follows from the slope of measured calibration curves or from the theoretical slope of 59.2 mV/decade. If only small deviations in potential are considered (in the range of only a few mV), it can be calculated that an error in potential of 1 mV results in a relative error in chloride concentration of ca. 4 percent [4].

Several phenomena have been identified to disturb accurate measurements of sensor potentials when measuring in cement based materials [5]. When an external reference electrode is used by establishing contact to the concrete surface with a wetted sponge the situation can be schematically depicted as in Fig. 1. Several components contribute to the measured potential, namely the *liquid junction potential* at the interface between inner solution of the reference electrode and the wetting agent in the sponge  $E_{RE-S}$ , the *liquid junction potential* at the boundary between the wetting agent in the sponge and the concrete pore solution  $E_{S-C}$ , as well as *membrane potentials*  $E_C$  across the concrete, and eventually *iR drops*. Both liquid junction and membrane potentials are all so-called *diffusion potentials* and arise due to concentration gradients in combination with differences in mobility between the diffusing ions. The significance of diffusion potentials for electrochemical measurements in concrete has been recently discussed by the author in ref. [5].



**Fig. 1. Disturbing phenomena when measuring potentials in concrete**

### *Consequences for experimental setups*

In order to measure reliable free chloride contents in concrete with potentiometric sensors one has to be very careful with regard to the setup. Liquid junction potentials at the interface between an external reference electrode and the sample surface can be minimised (but never completely avoided) if the reference electrode is contacted to the concrete with an appropriate solution [5]. With regard to membrane potentials the position of the reference electrode appears to be decisive: To minimise contributions from membrane potentials arising from internal concentration gradients the reference electrode should ideally be placed at the same depth as the chloride sensors (e.g. by use of embedded reference electrodes).

## Conclusions

The following sums up the current project plans and the results obtained so far:

- The current project aims at using a practice-related testing setup for determining the critical chloride content in dense concrete, based on both free chloride and total chloride contents.
- Ag/AgCl electrodes can be used as ion selective electrodes embedded in concrete to measure the free chloride content non-destructively. However, the technique is highly sensitive to errors in potential measurements arising from phenomena such as diffusion potentials. This is not a problem of the sensor itself, but of potential measurements through concrete as such.

## References

1. U. Angst and Ø. Vennesland. Critical chloride content in concrete - state of the art. In *2nd Int. Conf. on Concrete Repair, Rehabilitation and Retrofitting*. Cape Town, South Africa. 2008, (accepted for publication).
2. R. Cigna, C. Andrade, U. Nürnberger, R. Polder, R. Weydert and E. Seitz, ed. *COST 521: Final report "Corrosion of steel in reinforced concrete structures"*. Luxembourg, 2002.
3. B. Elsener, L. Zimmermann and H. Böhni. Non destructive determination of the free chloride content in cement based materials. *Materials and Corrosion* 54 (2003), 440-446.
4. J. Koryta. Theory and applications of ion-selective electrodes. *Analytica Chimica Acta* 61 (1972), 329-411.
5. U. Angst, Ø. Vennesland and R. Myrdal. Diffusion potentials as source of error in electrochemical measurements in concrete. *Materials and Structures* (2008), (in press. DOI:10.1617/s11527-008-9387-5).





COIN Workshop on Critical Chloride Content in Reinforced Concrete  
5–6 June 2008, Trondheim

## Laboratory experiments for detecting critical chloride content in reinforced concrete

Ueli Angst  
PhD Candidate at NTNU  
Norwegian University of Science and Technology

### Overview – my project

#### Part I

- Brief background and motivation for my project
- My plans and aims
- Expected results

#### Part II

- Results so far

## Critical chloride content $C_{crit}$ – State of the Art

Literature evaluation:

### Large scatter in reported results

0.02...3.04% total chloride by weight of cement

Different **definitions** used

Different **measurement techniques** used

A lot of **influencing parameters** on critical chloride content

- such as:
- pH of the pore solution
  - Steel-concrete interface
  - Potential of the steel
  - Moisture content
  - etc

## Critical chloride content $C_{crit}$ – State of the Art (2)

A lot of studies have already been undertaken on this topic...

...on **steel bars in solution** or **steel in cement paste / mortar / concrete**

...under **laboratory conditions** or **outdoor exposure**

...with **mixed-in chloride** or **chloride ingress by capillary suction** and/or **diffusion** or **migration**

...with **smooth** or **ribbed** steel bars

...with **polished** or **sandblasted** or **cleaned** or **pre-rusted** or **as-received** rebars

...by measuring **total** or **free** chloride contents or **Cl<sup>-</sup>/OH<sup>-</sup>** ratios

➡ Main outcome:

- Extremely **large scatter** in the results
- Major **influencing factors** identified (see slide above)

## Critical chloride content $C_{crit}$ – State of the Art (2)

A lot of studies have already been undertaken on this topic...

...on **steel bars in solution** or **steel in cement paste / mortar / concrete**

...under **laboratory conditions** or **outdoor exposure**

...with **mixed-in chloride** or **chloride ingress by capillary suction** and/or **diffusion** or **migration**

...with **smooth** or **ribbed** steel bars

...with **polished** or **sandblasted** or **cleaned** or **pre-rusted** or **as-received** rebars

...by measuring **total** or **free** chloride contents or **Cl<sup>-</sup>/OH<sup>-</sup>** ratios

→ Many studies were **not practice-related**

→ In the majority of the studies the **total chloride content** was measured; **Free chloride** thresholds were only reported in connection with **solutions** or **porous mortar / concrete**.

## State of the Art – Summary

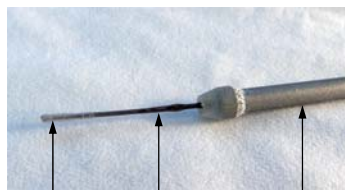
- **A lot of studies** have been undertaken using a **lot of different techniques** and **definitions**. The reported results **scatter** in a wide range.
- Most researchers reported **total chloride contents**; **free chloride** contents or **Cl<sup>-</sup>/OH<sup>-</sup>** ratios were reported in connection with **solution experiments** or **porous mortar/concrete**. There is a lack of results in the range of low porosity concrete and free chloride contents.
- Many studies were **not practice-related** (but indicated the major influencing factors).
- For the critical chloride content, **no standardised or accepted testing method** exists at present.
- Confusing results with regard to the **role of bound and free chlorides**. What is the role of bound chlorides in the corrosion initiation process?

## Plans and aims for my project

- Measure both the **free** and **total chloride content**...
  - **Role of bound and free chloride?**
  - **Form to express chloride threshold** favoured?
- ...in **dense concrete** (low w/c ratio)
- Non-destructive "**free chloride sensors**" (Ag/AgCl ion selective electrodes)
- **Practice-related testing method**

## Ion selective electrodes – chloride sensors

- Ag/AgCl electrodes for potentiometric chloride determination:



AgCl      AgCl coated silver wire      Stainless steel tube

Nernst's law:

$$E_{Ag/AgCl} = E_{Ag/AgCl}^o - \frac{RT}{F \log e} \log a_{Cl^-}$$

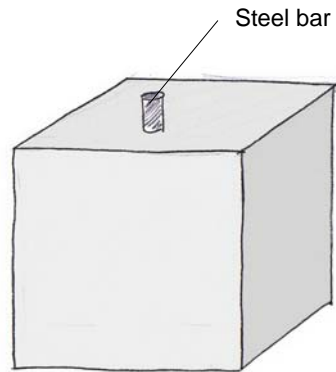


$$a_{Cl^-} = f(E_{Ag/AgCl}, T)$$

- Calibration in various media → **calibration curves**

## Experimental setup and procedure (1)

- Cast **concrete** cube with an embedded carbon **steel bar**



### Equipped with

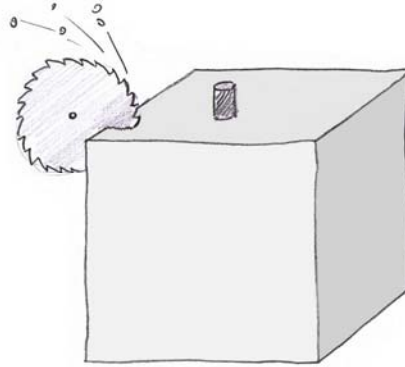
- Chloride sensors
- Embedded reference electrode(s)
- Stainless steel bar (counter electrode for LPR)

## How to get the chlorides into the concrete samples?

Technique	Pro	Contra
Mixed-in	<ul style="list-style-type: none"> <li>- Fast</li> <li>- Homogeneously distributed</li> <li>- Total chloride content well-known</li> </ul>	<ul style="list-style-type: none"> <li>- Initial formation of passive film questionable</li> <li>- Homogeneously distributed</li> <li>- Chloride binding different</li> <li>- Porosity affected</li> </ul>
Pure diffusion	<ul style="list-style-type: none"> <li>- Affinity to practice</li> </ul>	<ul style="list-style-type: none"> <li>- Very time consuming</li> <li>- Sample water saturated (limited oxygen availability)</li> </ul>
Capillary suction and diffusion	<ul style="list-style-type: none"> <li>- Affinity to practice</li> </ul>	<ul style="list-style-type: none"> <li>- Time-consuming</li> <li>- Initial drying for capillary suction might change the porosity</li> </ul>
Migration	<ul style="list-style-type: none"> <li>- Rather fast</li> </ul>	<ul style="list-style-type: none"> <li>- Current field</li> <li>- Migration of hydroxide ions (affecting pH in concrete)</li> <li>- Sample water saturated (limited oxygen availability)</li> </ul>

## Experimental setup and procedure (2)

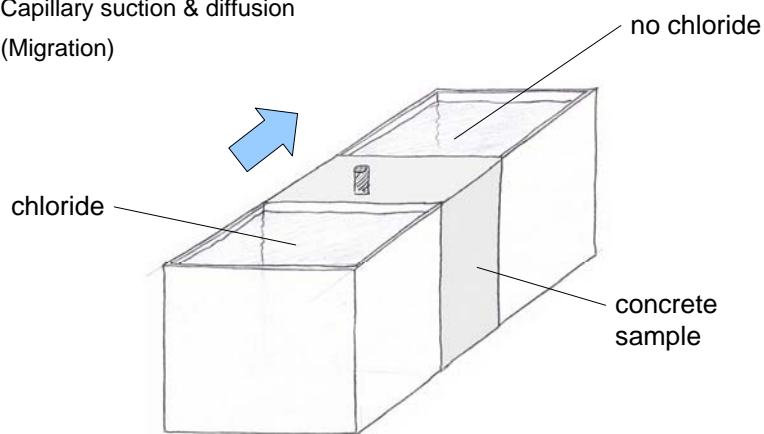
- After curing, cutting and/or grinding to **reduce the concrete cover**



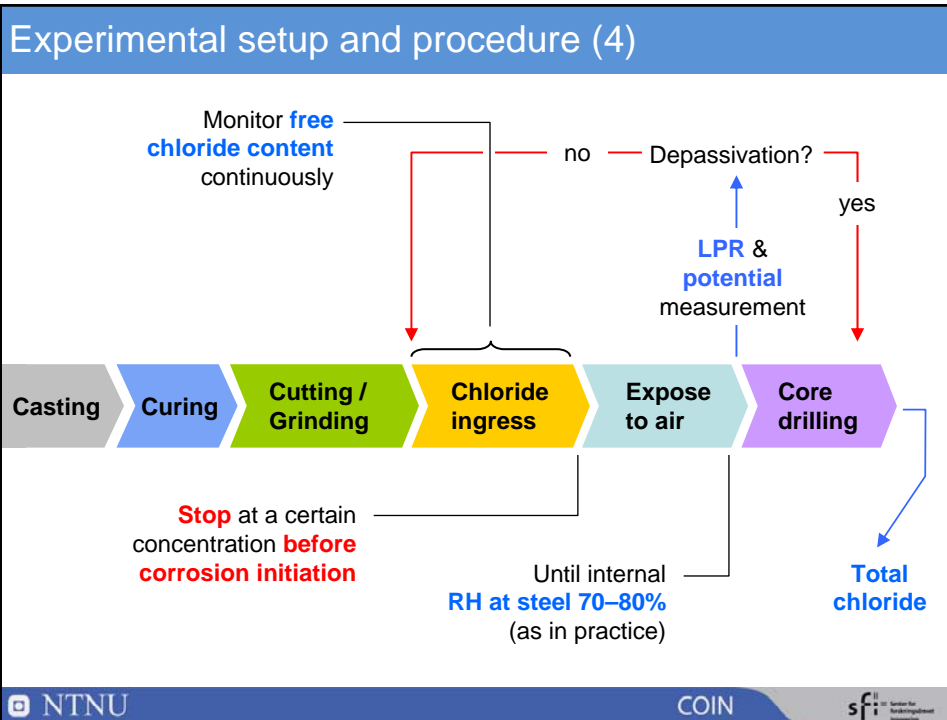
## Experimental setup and procedure (3)

### Chloride penetration

- Capillary suction & diffusion
- (Migration)



- Follow **free chloride concentration** with sensors






- ### Expected results
- Values for **critical chloride content** in...
    - ...**dense concrete**...
    - ...based on both the **free** and **total chloride content**
  - **Improved non-destructive measurement technique for the free chloride content** in concrete (embedded chloride sensors)
  - Suggestion for a **practice-related testing method**
    - Probably not for finding  $C_{crit}$  values for use in service life calculations; more as a testing method to compare different systems (rankings)
- NTNU COIN sfi



## Part II

### Results so far – Chloride sensors

### Calibration of Ag/AgCl electrodes in solution (1)

Setup: Ion selective electrodes in various solutions with known **chloride concentration**  
 Potential measured vs. sat. Calomel electrode (SCE)

Corrections:

- 1 **Activity vs. concentration**

$$E_{Ag/AgCl} = E_{Ag/AgCl}^o - \frac{RT}{F \log e} \log a_{Cl^-}$$




Cl<sup>-</sup>

➡

Activity coefficients
  
- 2 **Liquid junction potential** at boundary between SCE and solution
 

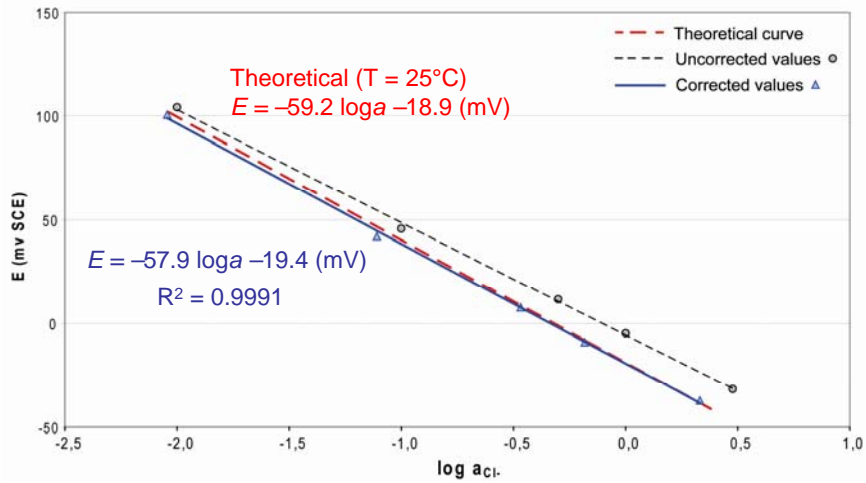
➡

Correct liquid junction potential error

## Calibration of Ag/AgCl electrodes in solution (2)

Calibration curves. Example for **synthetic pore solution**:

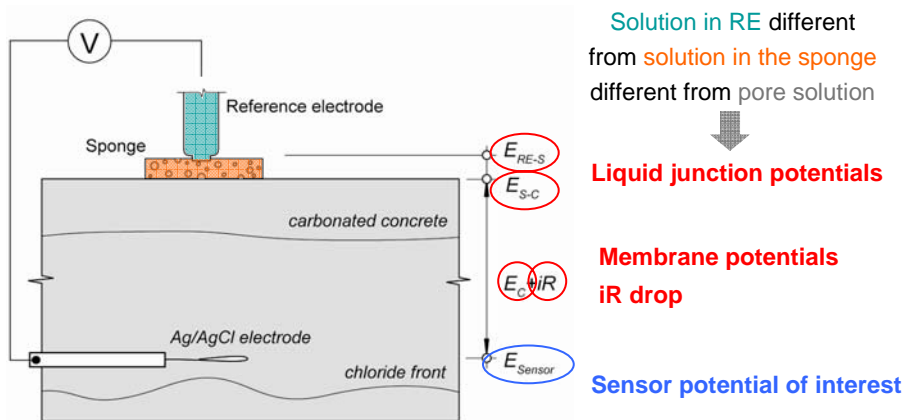


## Sensitivity & accuracy of Ag/AgCl electrodes

In direct potentiometry: 1 mV measurement error  $\approx$  4% error in chloride activity

➡ **Very accurate potential measurement required**

**Disturbing phenomena** for potential measurements in concrete:



## Diffusion potentials

Two solutions of **different composition** in contact → » Liquid junction «

Diffusion takes place

Diffusing ions have **different mobilities**

↓

Different **diffusion rate**

↓

Charge separation

↓

Electric field  $E_d$

↓

$E_d$  accelerates the slow ions and holds back the fast ions

**Steady state**

Potential difference across the boundary

↓

» Diffusion potential «

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## Diffusion potentials – Henderson equation

Two solutions of **different composition** in contact → » Liquid junction «

↓

» Diffusion potential «

**Henderson equation:**

$$E_d = \frac{RT}{F} \frac{\sum \frac{|z_i|}{z_i} u_i (c_i^\beta - c_i^\alpha)}{\sum u_i |z_i| (c_i^\beta - c_i^\alpha)} \ln \frac{\sum u_i |z_i| c_i^\alpha}{\sum u_i |z_i| c_i^\beta}$$

→ Estimate diffusion potentials


Assumptions:

- linear concentration gradients
- mobility independent of concentration
- concentration equivalent to activity

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## Diffusion potentials – Definitions

Two solutions of different composition in contact



**α**      **β**

Contact?

Cement paste

Pore walls / double layer affects mobility

$$D_{Cl^-} \gg D_{Na^+}$$

**Non-selective**

(diaphragm, e.g. porous frit)

↓

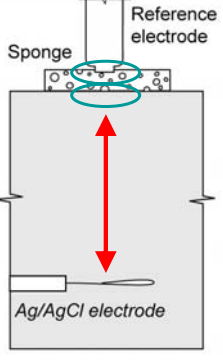
» Liquid junction potentials «

**Permselective**

(permeable for some, but impermeable for other substances)

↓

» Membrane potentials «



Sponge

Reference electrode

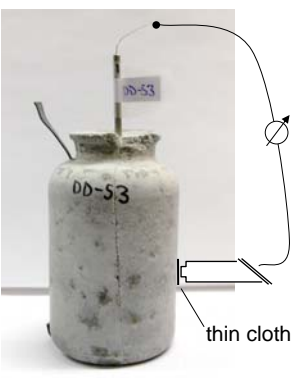
Ag/AgCl electrode

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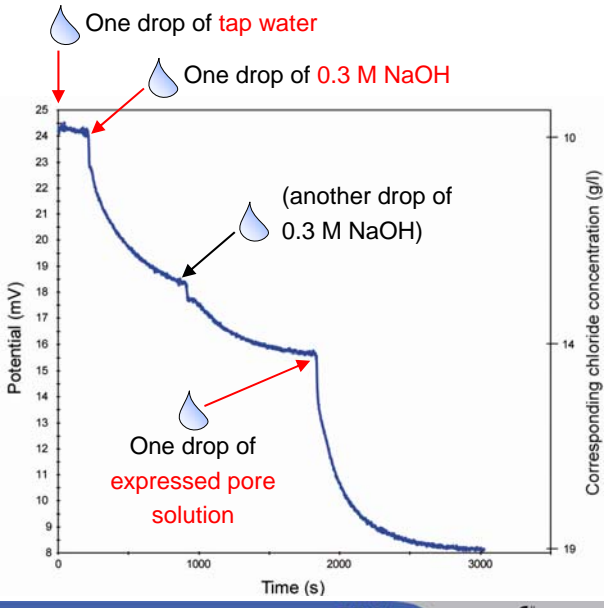
## How diffusion potentials affect measurements (1)

Mortar sample with embedded  $Cl^-$  sensor

Admixed chloride: 2% per cem wt



thin cloth



One drop of tap water

One drop of 0.3 M NaOH

(another drop of 0.3 M NaOH)

One drop of expressed pore solution

Potential (mV)

Time (s)

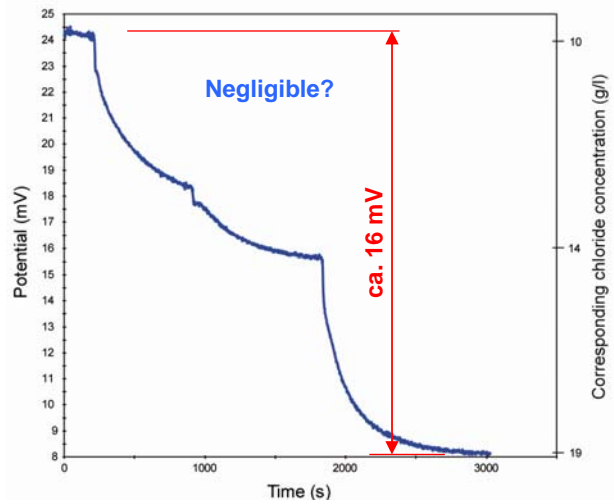
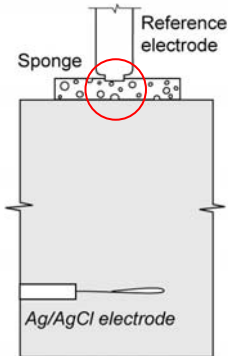
Corresponding chloride concentration (g/l)

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## How diffusion potentials affect measurements (2)

In direct potentiometry: 1 mV measurement error  $\approx$  4% error in chloride activity

### Liquid junction potentials

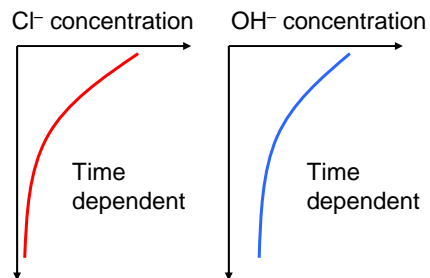
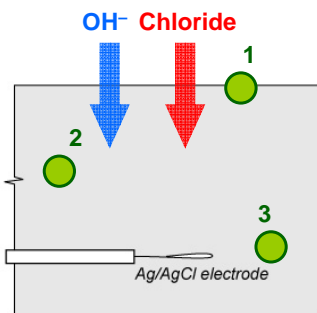


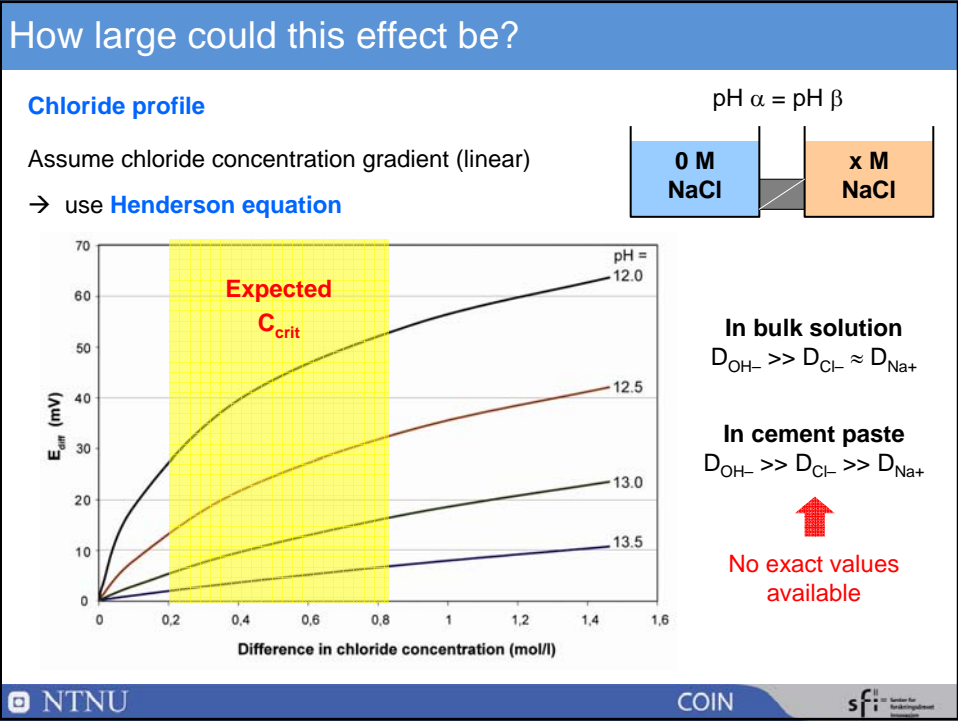
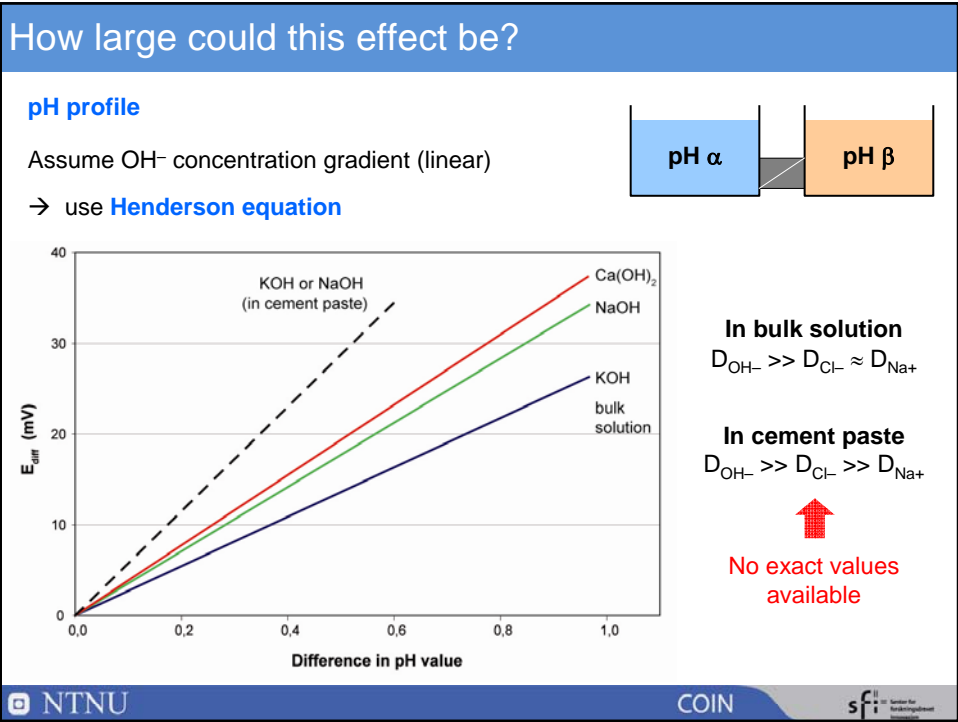
## What does this mean for my setup?

Chloride ingress from surface  $\rightarrow$  **chloride profile**

In case of migration  $\rightarrow$  **OH<sup>-</sup> concentration profile**

Where to place the **reference electrode**?



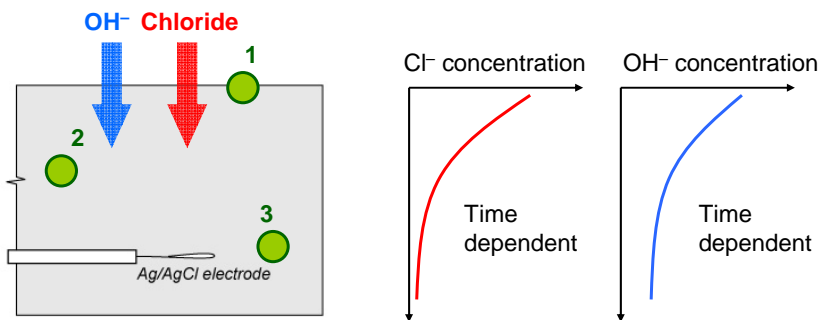


## What does this mean for my setup?

Impossible to calculate membrane potentials along concentration profiles in concrete accurately; pH profiles are presumably more serious than chloride profiles.

These phenomena are a **serious error source** for the measurement.

➡ Position of the **reference electrode** is very important.



## Comparison with pore solution expression

Three parallel mortar samples (2% total chloride by cem wt)

Measured **potential of chloride sensors**: 8 – 12 mV vs ext. SCE

Calibration curve  
and corrections  
(liquid junction, activity)

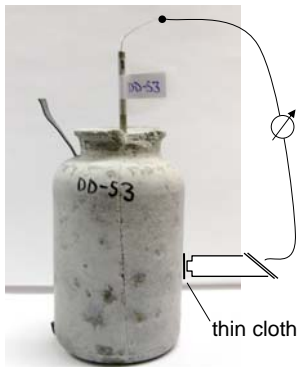
**Concentration = 0.5 mol/l**

**But:** pore solution expression → 0.75 mol/l

Possible reasons:

- Membrane potentials?
- Activity affected by the pore walls?
- Pressure increases free Cl<sup>-</sup>?

→ More experiments to answer this.



## Conclusions for the use of chloride sensors

- **Direct potentiometry is very sensitive.**
- **Chloride sensors** (Ag/AgCl electrodes) can be used to measure the **free chloride content in concrete** non-destructively.
- **But**, one has to...
  - Be careful with what solution is used to **contact the concrete surface**
  - Be careful with the **position of the reference electrode (RE)**
  - **Avoid pH gradients** and **chloride concentration gradients** between the RE and the chloride sensor

Thank you for your attention.





## **7 Critical chloride content and concrete resistivity**

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### **“Critical chloride content for reinforced concrete and its relationship to concrete resistivity”**

*Rob B. Polder*

*TNO*



## Critical chloride content for reinforced concrete and its relationship to concrete resistivity

Dr. Rob B. Polder, TNO Built Environment and Geosciences, Delft, The Netherlands

COIN Workshop on Critical Chloride Content in Reinforced Concrete, NTNU, June 5-6, 2008

### Introduction: Problematic issues

Service life design (including re-design or assessment) of reinforced and prestressed concrete structures requires a number of input variables. One of the variables that is difficult to quantify is the critical chloride content or threshold value. This is due to issues of:

- concept and definition
- experimental parameters
- measuring method
- influences in the field.

In engineering terms, the underlying concept is that no or low (insignificant) corrosion of embedded reinforcing (or prestressing) steel occurs at chloride contents below the critical content; significant corrosion occurs above the critical value. Under external chloride load, the content at the bar surface increases over time and at some point, a transition takes place from absence to presence of corrosion, or, in electrochemical terms, from passive to active.

Definitions for the critical value usually refer to:

- the transition from passive to active (onset of corrosion)
- an unacceptable amount of damage (usually of concrete cracking and spalling).

The "active-passive" definition is problematic from the point of view of measuring methods and criteria. Some effect of reaching the critical level at a reinforcing bar should be measurable; and next, the effect should be significant. For instance, a drop of steel potential may not be due to corrosion initiation but to reduced oxygen access. In any case, this definition provides the best option to proceed; see below.

The "unacceptable" definition is problematic because it cannot be generalised; it is based on management policies and lies outside the realm of materials science. A rational approach of acceptable damage-due-to-corrosion-due-to-chloride could be based on reliability (safety) or risk (economy) considerations; thus, individual owners may use different levels of acceptability.

The introduction of reliability or more generally probabilistic considerations is very useful, though. Initiation and pitting corrosion are stochastic processes, e.g. as demonstrated by electrochemical noise measurements. Moreover, various influences on corrosion initiation and critical content may have considerable spatial variation, e.g. the density of the cement paste or the presence of aggregate particles and air voids near the steel surface. Others vary in time, either periodically or continuously, such as temperature, moisture content and pH changes. Field studies have shown that the probability of corrosion increases with the chloride content at the depth of the steel (Vassie, Everett).

Sometimes a third "definition" is used: the acceptable amount of chloride in the fresh concrete as given by Standards. This is not a proper definition, however, as it includes an unknown

safety margin and as the effect of mixed-in chloride on passivation and corrosion is different from that of penetrated chloride.

### Practical solutions

Andrade and a group within COST 521 have proposed that depassivation is a process that takes a certain amount of time, at the end of which corrosion has been firmly established. Thus, the critical content can be defined as the value above which a sustained corrosion rate of more than  $1 \text{ mA/m}^2$  (c.  $1 \text{ }\mu\text{m/year}$ ) occurs. Advantages of this definition are that the corrosion rate is directly related to the cross section loss and that it is measurable, at least in principle. For experimental determination, a test setup has to be found that must address several problematic issues:

- exposure (moisture content, temperature, oxygen access)
- compositional and interfacial factors (cement type and content, w/c, aggregate, air voids, steel surface properties)
- electrochemical effects (free or imposed potential, cathodic area, measuring method, e.g. polarisation resistance, macro cell current)
- high precision of measuring methods
- and finally, statistical treatment of the results.

Breit has succeeded in solving most issues, providing the basis for a statistical expression of the critical content. From his experiments on mainly ordinary Portland cement materials, the critical level has a mean of about 0.5% by mass of cement with a standard deviation of about 0.2%. The type of distribution is slightly problematic, though: it could be normal, lognormal or beta. This is due to the relatively low number of results at the low end, where the probability is low but significant. Nowadays, service life design aims at a probability of corrosion (initiation) of 10% or less. So, a practical solution could be accepting Breit's mean and standard deviation; in the author's opinion, a lognormal distribution provides the best fit to the low end and should be chosen.

### Analysis of another data set

A large number of data was obtained from specimens with penetrated chloride and embedded electrodes for corrosion potential, polarisation resistance and concrete resistivity measurements (Polder). These data are analysed in view of the discussion given above.

### Further research needed

Usable data on the critical chloride content including statistical parameters appears to be available, in particular for ordinary Portland cement concrete, although the actual distribution at the low but critical end is still open for debate. Remaining questions regard the influence of blending agents (slag, fly ash, silica fume) and the effect of lower binder contents which are desirable from the point of view of raw materials and energy conservation. A simple test method that can produce good statistical information needs to be designed and tested. Finally, confirmation from field data is needed.

### References

Andrade, C., et al., section 2.4 in: COST 521, 2003, Corrosion of steel in reinforced concrete structures, Final Report, Eds. R. Cigna, C. Andrade, U. Nürnberger, R. Polder, R. Weydert, E.

Seitz, European Commission, Directorate-General for Research, EUR 20599, ISBN 92-894-4827-X, 238 pp.

Breit W., 2001, Critical corrosion inducing chloride content – State of the art and new investigation results, *Betontechnische Berichte 1998 - 2000*, Verein Deutscher Zementwerke e.V., Verlag Bau+Technik, Düsseldorf, 145-167

Everett, L.H., Treadaway, K.W.J., 1980, Deterioration due to corrosion in reinforced concrete – BRE Information IP12/80, Building Research Establishment

Polder, R.B., Peelen, W.H.A., Bertolini, L., Guerrieri, M., 2002, Corrosion rate of rebars from linear polarization resistance and destructive analysis in blended cement concrete after chloride loading, 15<sup>th</sup> International Corrosion Congress, Granada, September 22 – 27

Vassie, P.R., 1984, Reinforcement corrosion and the durability of concrete bridges, *Proceedings of the Institution of Civil Engineers, Part 1, Vol. 76*, paper 8798, 713



# Critical chloride content for reinforced concrete and its relationship to concrete resistivity

Rob Polder

TNO | Knowledge for business



## Contents

- Ccrit general remarks
- Experiments
- Discussion
- Conclusions





## Ccrit general remarks

- Service life design modelling; need input variables
- Ccrit problematic
  - Concept, definition
  - Experimental parameters
  - Measuring method
  - Field influences
- Concept
  - $CI < C_{crit}$  negligible corrosion
  - $CI > C_{crit}$  significant corrosion
- Definition
  - Transition: passive -> active
  - Unacceptable amount of damage
  - Allowed by Standards (fresh concrete)

3

Ccrit and resistivity

NTNU/COIN June 2008

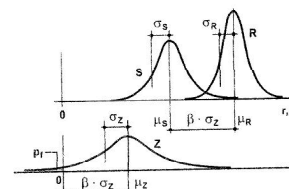


## (un)acceptable amount of damage

- Over which time?
- Management policy (owner dependent), not materials science issue!
- Should be based on reliability or risk of damage...
- Risk = Cost \* probability



- Probability useful concept
- Corrosion (initiation), load, concrete stochastic
- Prob(corrosion) increases with CI (BRE, Vassie, 1980s), e.g. 0.4 -> 1% (binder)
- Ccrit = statistical distribution!
- Most interesting: Low Prob!



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Ccrit and resistivity

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## Allowed by Standards in fresh concrete

- Safety margin unknown
- 0.4% reinforced, 0.2% prestressed
- used to be 0.3 and 0.1%!
- Economically negotiated values
- Effect mixed in CI  $\neq$  penetrated CI



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Ccrit and resistivity

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## Transition: passive -> active

- COST 521 (ao Andrade, Frederiksen, Glass, Page)
- *Initiation = process (takes time)*
- *Ccrit: sustained CR > 1 mA/m<sup>2</sup>*
- Measurable.. but
  - Accuracy moderate > 2 mA/m<sup>2</sup>
  - Exposure (T, H<sub>2</sub>O, O<sub>2</sub>)
  - Concrete/mortar (cement, w/c, air voids, steel surface)
  - Potential, cathodic area..
  - Statistical treatment



6

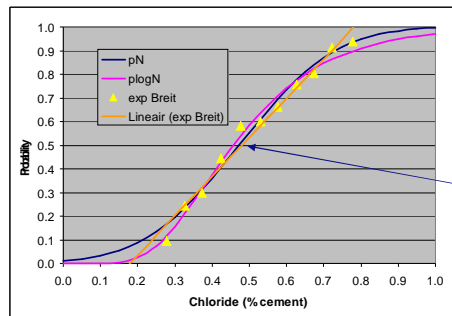
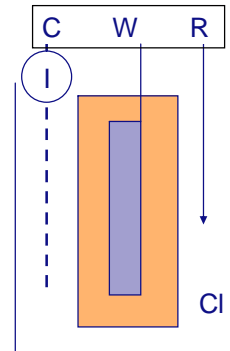
Ccrit and resistivity

NTNU/COIN June 2008

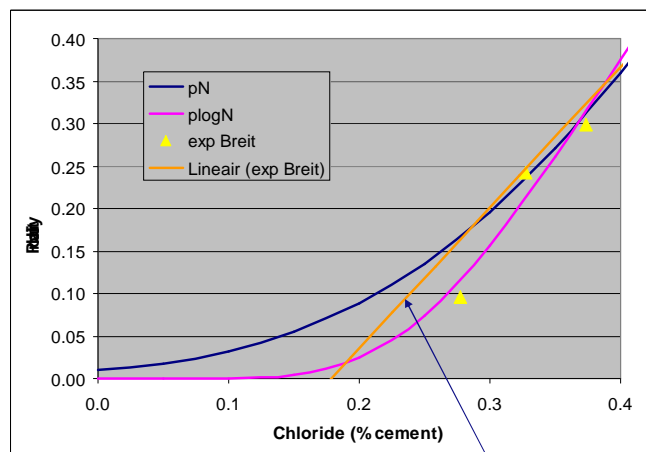


## Example: Breit 2001

- E 0.5 V(H), migrate Cl, Monitor I(t),
- I=0 passive
- I>0 active, stop experiment
- Split specimen, take out steel
- Reassemble, drill dust in hole (1 mm), test Cl
- Mortar, 11 comp., 5 binders



Mean c. 0.5%



10% value depends on type/fit

- Type of Distribution!
- Low end! 5..10% probability of corrosion
- Mean 0.5%; std 0.2%, logNormal



## Experiments TNO

- Chloride and corrosion rate (COST 521 project NL-2)
- Accelerated penetration, blended cements
- Monitor CR(LPR), Esteel, Resistivity; test Cl(x,t)
- 1 week fog room; 3 weeks 20C 80%RH
- Salt loading/drying: week 5 - 30, 1st chloride profile (n=6/mix)
- Three climates: week 31 – 130
  - Fog room (n=2/mix)
  - Outside unsheltered (n=2)
  - 20°C 80%RH (n=2)
  - week 130 2nd chloride profile (n=3/mix\*)

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Ccrit and resistivity

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## Compositions $D_{max}$ 8 mm X = test destr. 130 weeks

	water-to-cement ratio	0.40	0.45	0.55
cement				
CEM I 32.5 R Portland cement		x	x	x
CEM II/B-V 32.5 R Portland fly ash cement, 27% fly ash			x	x
CEM III/B 42.5N LH HS Blast furnace slag cement, 75% slag				x
CEM V/A 42.5N Composite cement, 25% fly ash & 25% slag				x
cement content (kg/m <sup>3</sup> )		336	318	283

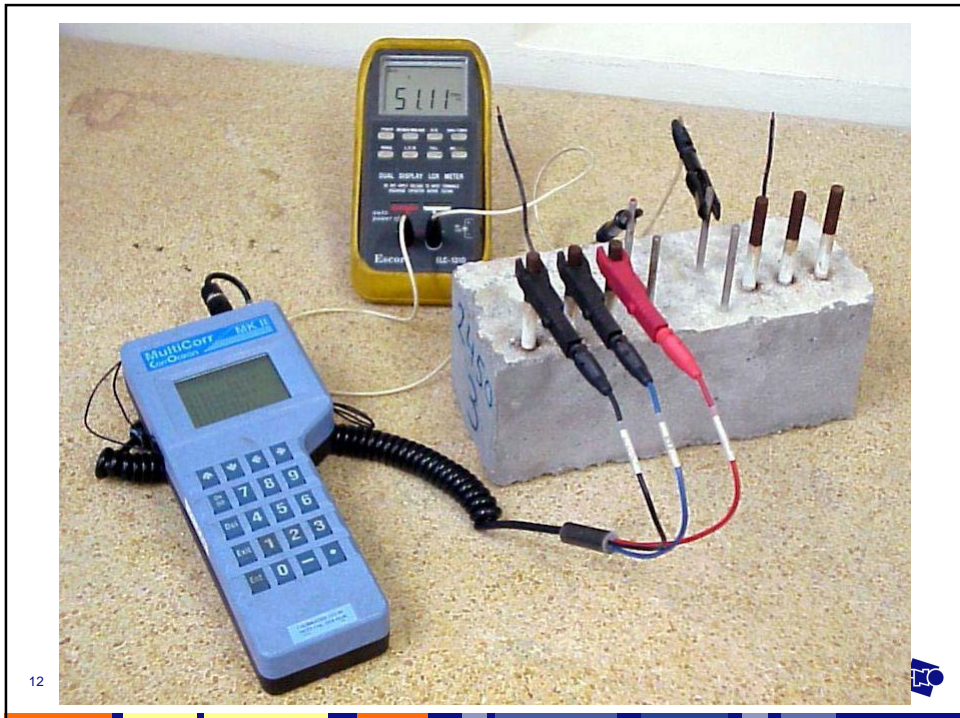
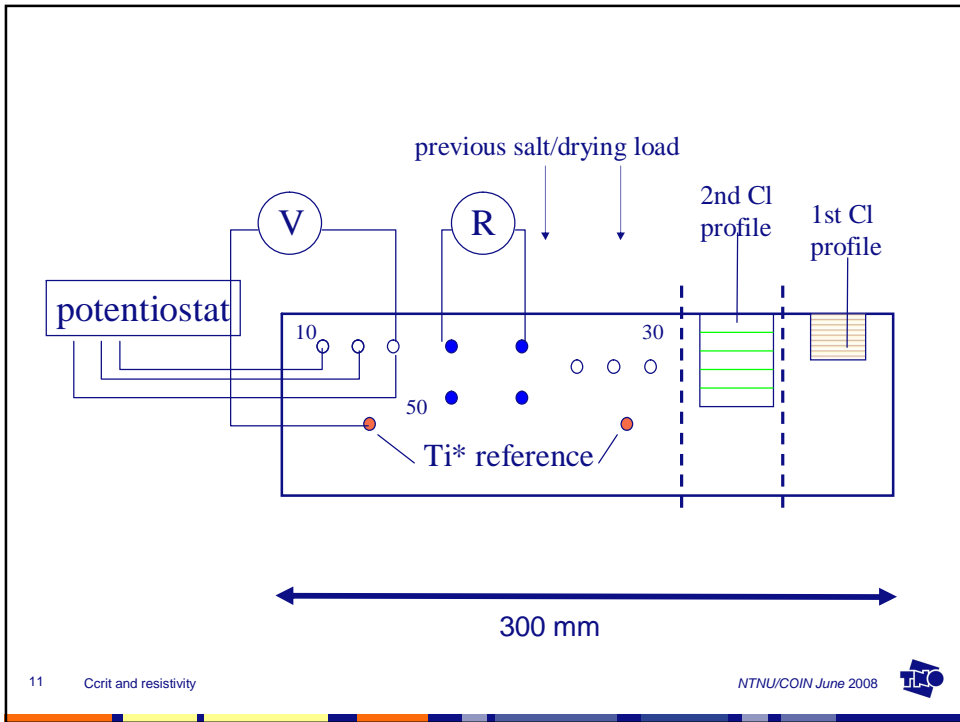
> Considerable amount of air voids (~practice....)

10

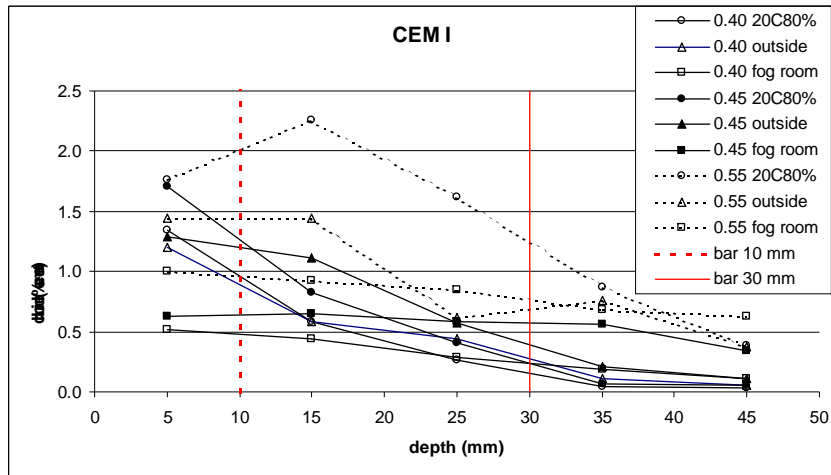
Ccrit and resistivity

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## 2nd CI profiles at 130 weeks



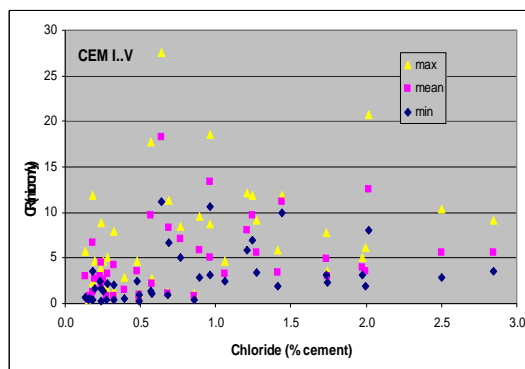
13 Crit and resistivity

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## Results

- 130 weeks: CI(1), CR(3), Res(1); for  $x = 10, 30$  mm
- ! Fog room, outside, 20C 80%RH; CEM I, II/B-V, III/B, V/A; w/c
- CI(10/30) 0.1 .. 3%
- CR(10/30) 0 .. 30  $\mu\text{m}/\text{y}$
- All data fit problematic..
- $\text{CR} = 1.9 \text{CI} + 3.0$  ( $R^2=0.11$ )
- Separate CEM, exposure



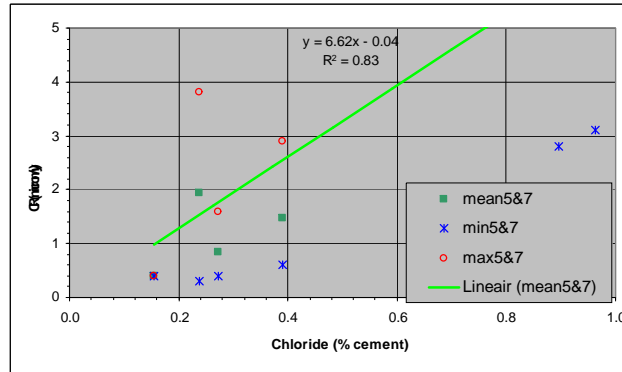
14 Crit and resistivity

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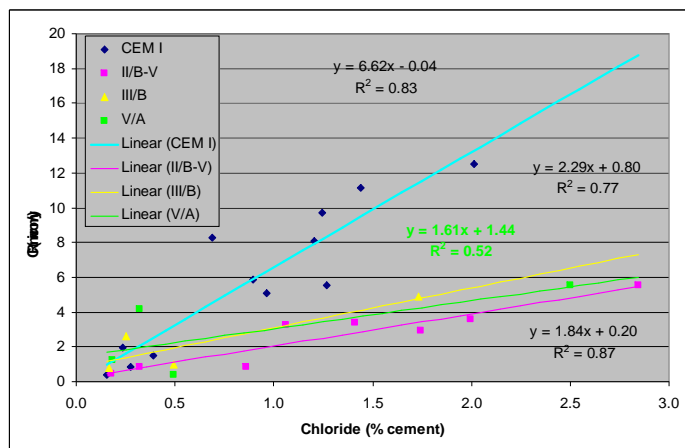
## CEM I, 20C 80%RH, outside (6 spec., 36 bars)

- **CR = 6.62 Cl - 0.04 (R<sup>2</sup>=0.83)**
- Cl = 0% <-> CR = 0 μm/y
- CR = 1 μm/y <-> Cl = 0.16%
- CR = 2 μm/y <-> Cl = 0.31%
- CR = 5 μm/y <-> Cl = 0.76%
- needs further statistical treatment!



15 Ccrit and resistivity

## CEM II/B-V; III/B; V-A; 20C 80%RH, outside



CEM I

CEM II..V

16 Ccrit and resistivity

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## Overview CEM I .. V; CI(CR) (% binder)

CR ( $\mu\text{m}/\text{y}$ )	1	2	5
CEM I	<b>0.16</b>	<b>0.31</b>	<b>0.76</b>
CEM II/B-V fly ash	0.43	0.98	2.6
CEM III/B slag	0.09	0.52	1.8
CEM V/A fly ash & slag	-	0.35	2.2

OK

Transition of control?

Bad fit..

CEM (II,) III, V: n = low; further study



Steel potential:

if negative; some low, some high CR;  
if positive: low CR

Corrosion rate =  $f(\text{Cl}, \text{wetness}; \text{cement})$

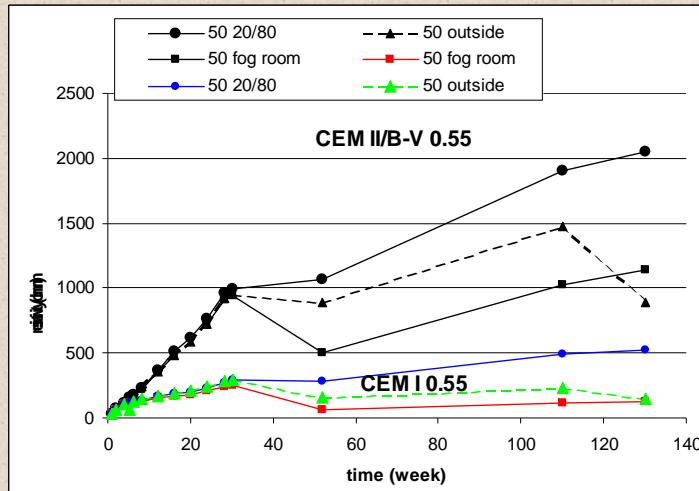
CR ( $\mu\text{m}/\text{year}$ , mean) in 3 climates, wk 52-130

w/c cement	0.40	0.45	0.55
CEM I	1 - 5	2 - 10	5 - 15
CEM II/B-V		1 - 5	1 - 5
CEM III/B			1 - 6
CEM V/A			1 - 5

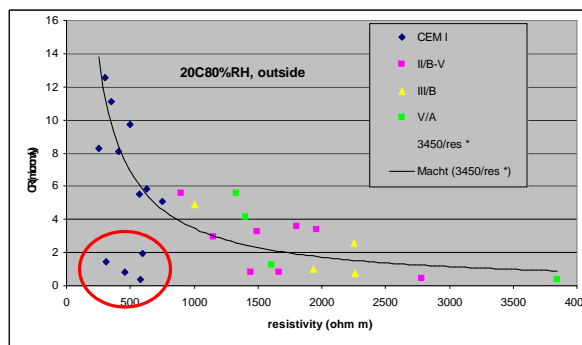




## Concrete resistivity



## Resistivity control?



- $CR=f(Res)$  for  $Cl \gg C_{crit}$



## Resistivity results "bulk" 30-130 week

w/c	0.40	0.45	0.55
CEM			
I	190	160	110
II/B-V		1200	1000
III/B			1600
V/A			1300

Fog room

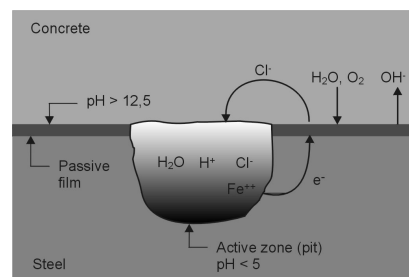
w/c	0.40	0.45	0.55
CEM			
I	500	450	380
II/B-V		2200	1700
III/B			2000
V/A			2700

Outside, 20°C 80%RH



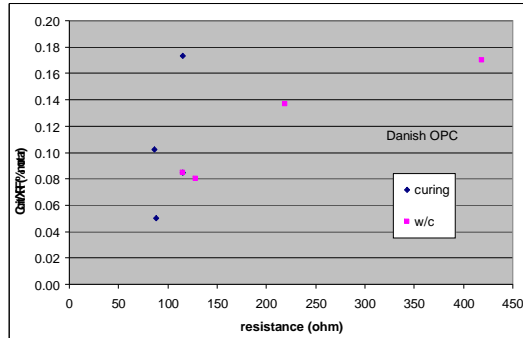
## Ccrit & resistivity, "if any"

- Nature of Ccrit?
- Not thermodynamic
- Kinetic; breaks down passive film
- Pit:  $\text{Cl}^- \uparrow$ ,  $\text{pH} \downarrow$
- Concentration & transport of Cl
- Cl transport ~ resistivity
- But: also OH transport ~...



## Hansson & Sørensen, 1990

- E 0.0 V SCE, migrate Cl until  $I_a \gg 0.1 \text{ mA/m}^2$
- $t_i$ , Cl@steel, resistance ( $\Omega$ )
- various binders, w/c, curing
- +fly ash: high resistivity, same Ccrit ( $t_i$  longer..)
- w/c effect; Ccrit ~ resistivity !
- Curing effect; Ccrit not ~,,
- -> ?????
- origin of resistivity..

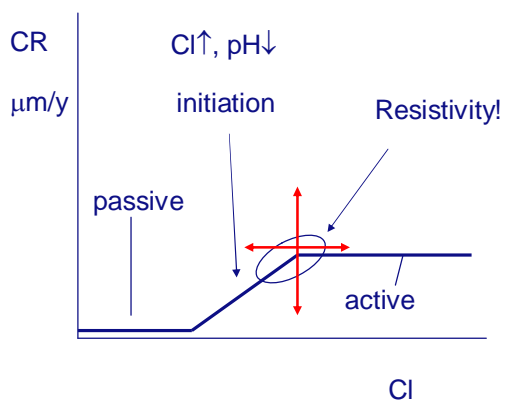


23 Ccrit and resistivity

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## Initiation model



24 Ccrit and resistivity

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## Conclusions

- Service life design: requires Ccrit
- Need distribution
- Target probability 1 .. 5 .. 10%: low end!!
  
- Need clear relationship
  - Concrete composition
  - Exposure
  - Execution (compaction, curing)
  
- Methods: Est **X**; CR useful
  
- Resistivity decreases
  - w/c 0.40 > 0.45 > 0.55 influence on Ccrit!
  - slag>composite>fly ash>Portland cement (?)
  - 20°C80%RH > outside > fog room (?)
  - *Anyone for further study of old results?*





## **8 Critical considerations regarding laboratory research**

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### **“Critical considerations regarding laboratory research on the critical chloride content in reinforced concrete”**

*Joost Gulikers*

*Rijkswaterstaat Bouwdiens*



## **CRITICAL CONSIDERATIONS REGARDING LABORATORY RESEARCH ON THE CRITICAL CHLORIDE CONTENT IN REINFORCED CONCRETE**

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### Introduction

There is a general acceptance that the so-called critical chloride content,  $C_{crit}$ , is one of the key parameters to estimate service life for new as well as existing reinforced concrete structures exposed to chloride-laden environments. Consequently a strong practical need emerges to have a better understanding of the mechanisms involved in chloride-induced corrosion as well as to obtain more reliable values for  $C_{crit}$ . This renewed attention for the critical chloride content has resulted in a number of initiatives to perform laboratory investigations on a scientific level. However, the experience with previous laboratory research activities indicates that the test set-up does not reflect realistic conditions as commonly observed in practice. In view of that the practical significance of the outcome of such a laboratory research can be questioned.

### Laboratory practice versus site conditions

#### **Time constraints**

One of the major boundary conditions in laboratory research is that results should be available within a timeframe of less than 3 years. Consequently, a number of concessions is made as to achieve this. Most often chlorides are introduced in the fresh concrete mix in contrast to realcrete where chloride ions have to diffuse through the pore system of the concrete cover for a period of several decades before they reach the level of the reinforcing steel. This has 4 significant implications:

- for corrosion initiation the so-called free chloride content is of importance. The use of mixed-in chlorides will result in a higher amount of chlorides to be chemically bound by the cement hydration products. Thus a lower free chloride content will be encountered in the pore solution resulting in a higher critical chloride content.
- generally the chlorides are introduced in the mixing water and this results in a uniform chloride distribution through the concrete material. However, in realcrete a non-uniform chloride distribution will prevail and this provides a more favourable condition for inducing potential differences along the steel surface which is one of the major reasons for corrosion-initiation.
- the use of dissolved chloride in the mixing water accelerates the hydration process resulting in a coarser pore structure as compared to realcrete without admixed chlorides.
- most often chlorides are dissolved in such an amount as to allow for initiation of steel corrosion from the very beginning, i.e. even before the concrete has hardened. The reinforcement steel embedded in realcrete is given sufficient time to passivate and will



remain in this passive condition during many decades. In contrast to labcrete a passivating layer has to be attacked in real structures.

### **Geometrical constraints**

For practical reasons it is common in laboratory research to employ small size specimens having a relatively shallow cover and containing a single rebar. Chloride-induced corrosion is strongly localized and is thus accompanied by the formation of macro-corrosion cells. The short length of the embedded rebar may hinder the depassivation process as only a relatively small cathodic surface area is available to support anodic dissolution. For corrosion to occur potential differences should be promoted to occur along the steel surface. However, in laboratory research the concrete cover will be of uniform thickness and the steel surface thoroughly cleaned, sandblasted and degreased. These conditions are not likely to give rise to differential electrochemical behaviour. In addition, mortars rather than concrete is used in research. The presence of large aggregate particles in the concrete cover will result in a spatial variation of chloride, water and oxygen transport. Thus, some parts of the steel surface may be effectively shielded against penetration of deleterious substances, whereas in mortars the transport properties will be more homogeneous.

### **Structural constraints**

In real structures inadequate compaction and curing may have resulted in spatial differences in concrete quality, accompanied by surface cracking, gravel pockets and bleeding water. In addition, after loading, the steel reinforcement is under tension giving rise to flexural cracks extending from the exposed concrete surface to the embedded rebars. For higher stress levels the bond between concrete and steel may be severely compromised. As initiation of corrosion is strongly dependent on the quality of the steel-concrete interface, the critical chloride content in the flexural zone of a structure could be completely different from that in the compressive zone. Thus it would also be likely that in prestressed concrete structures in the absence of major cracking, the critical chloride content could be significantly higher.

### Concluding remarks

Many factors may impact the eventual level of the critical chloride content in real structures. In this respect laboratory research may not be adequate to assess the real level of  $C_{crit}$  in view of the time, geometrical and structural constraints outlined. In effect, additional factors that are not discussed here, may play an important role. In order to achieve results from laboratory research that are of practical relevance for real structures, the test set-up, specimen geometry, and exposure conditions should reflect outdoor conditions. In this respect long-term research using exposure sites in the vicinity of real structures could be of great help.

## **9 Critical chloride content and service life predictions**

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### **“Critical chloride content and its influence on service life predictions”**

*Gro Markeset*

*SINTEF*



## CRITICAL CHLORIDE CONTENT AND ITS INFLUENCE ON SERVICE LIFE PREDICTIONS

*Gro Markeset, Dr. ing.  
Project Manager, COIN - Concrete Innovation Centre  
SINTEF, Norway*

### INTRODUCTION

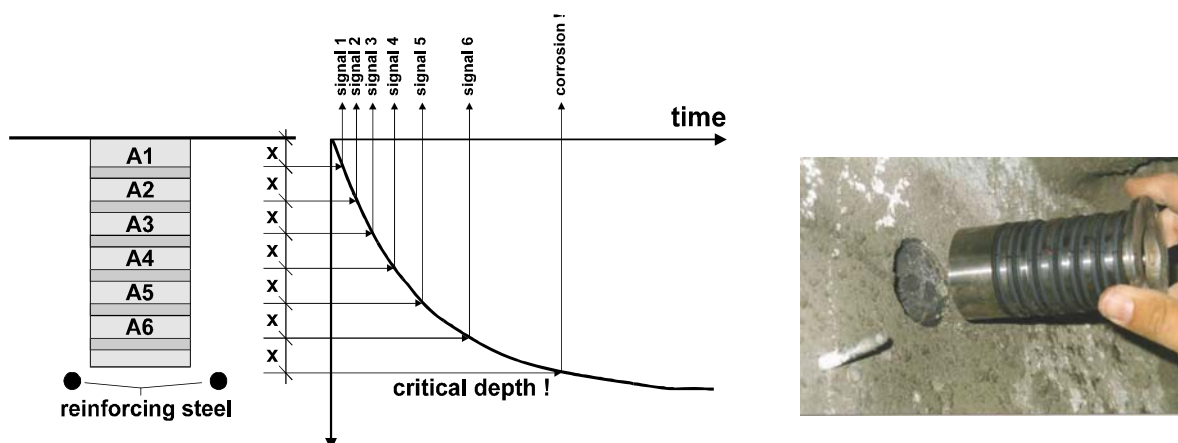
In the design of new concrete structures exposed to chloride induced corrosion the service life predictions are commonly based on the time to onset of corrosion. When the chloride content reaches a critical level at the depth of the reinforcement, the reinforcing steel becomes depassivated, and corrosion starts.

In service life modelling the critical chloride content (or the chloride threshold level) is required as input parameter. However, there is a lack of reliable data for this parameter, especially from field exposure of real structures

The wide scatter in observed chloride threshold values may, in addition to material and environmental factors, also be attributed to different measuring techniques and definitions of the threshold itself. For instance, some relate depassivation of the reinforcement to a certain shift in the corrosion potential, other use visual inspection of the reinforcement after chiselling, and finally, other relate depassivation with a certain level of the corrosion current.

### MEASURING CRITICAL CHLORIDE CONTENT IN REAL STRUCTURE

Installing corrosion sensors in existing structures exposed to chloride environments is one practical means of determining the chloride threshold value in an actual structure, see Figure 1. The basic measuring principle is to place steel electrodes into different depths related to the concrete surface and to measure the onset of corrosion of these electrodes one by one. The measuring electrodes are made of steel with a similar composition as reinforcing steel to ensure that they will start to corrode at the same time as a rebar at the same depth.



**Figure 1:** Basic principle to determine the time-to-corrosion (to the left) /1/. Mounting of corrosion sensors in existing quay (to the right). The small titanium pin as cathode placed just above the instrument

The corrosion monitoring system shows then directly the depth of the critical chloride content. The actual values of the critical chloride concentrations can be determined by comparing the chloride profile of the cores (drilled out for the placement of the sensors) with the level of corrosion currents for each sensor ring measured shortly after installation.

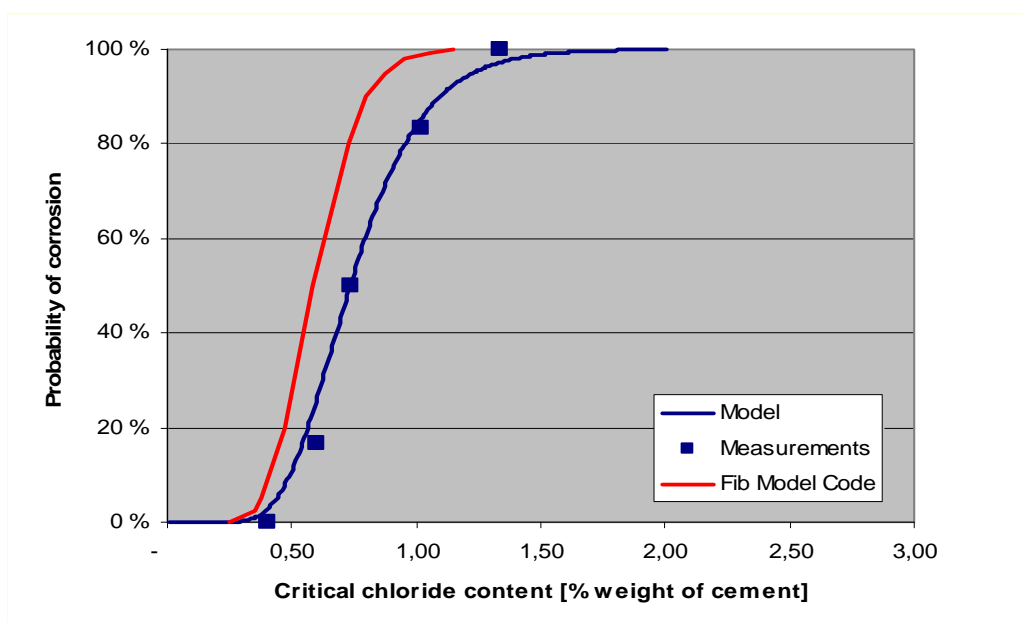
Such measurements have been performed on a 37 years old quay in the northern part of Norway /2/, based on 14 corrosion sensors installed above the tidal zone. The quay was made of a coarse-grained Portland cement. Based on petrographical analyses of the concrete the water/cement-ratio was found to vary between 0.40 and 0.50.

Due to the uncertainties in the measurements and variations among the corrosion sensors the critical chloride content is considered in terms of probability or risk of corrosion. The critical chloride contents obtained for the Norwegian quay are compared with Browne's classification of corrosion risk, see Table 1. A lognormal distribution is found to give the best fit to the measurements, giving a mean value for critical chloride content of 0.77 % weight of cement and a coefficient of variation equal to 32%, See Figure 2. It should be kept in mind that the corrosion sensors measure the time to depassivation (or at a very low level of corrosion current) and may therefore result in lower values than if the critical chloride content was based on visual inspection of the reinforcement after chiselling and identification of rust and corrosion. This might be the background for the high values suggested by Browne. In *fib* "Model Code for Service Life Design" /3/ a beta-distribution with mean value of 0.6 by % weight of cement is recommended, which is somewhat lower than found for the investigated quay, see Figure 2.

**Table 1:** Critical chloride content (% weight of cement)

Probability/risk of corrosion	Critical Chloride Content	
	According to Browne /4/	Norwegian quay /5/ *)
Negligible	<0.4	<0.4
Possible	0.4-1.0	0.4-0.7
Probable	1.0-2.0	0.7-1.3
Certain	>2.0	>1.3

\* assuming 350 kg cement/m<sup>3</sup> and density 2350 kg/m<sup>3</sup>



**Figure 2:** Critical chloride content: field data from a Norwegian quay and statistical model for these data /5/ compared with statistical model according to *fib* Model Code for Service Life Design /3/

## SERVICE LIFE PREDICTIONS

In probabilistic service life predictions of concrete structures exposed to marine environment, the critical chloride content is modelled as a stochastic variable characterized by a mean value, a standard deviation and a type of probability density function. The limit state function is defined as the difference between the critical chloride concentration and the calculated chloride concentration at the reinforcement:

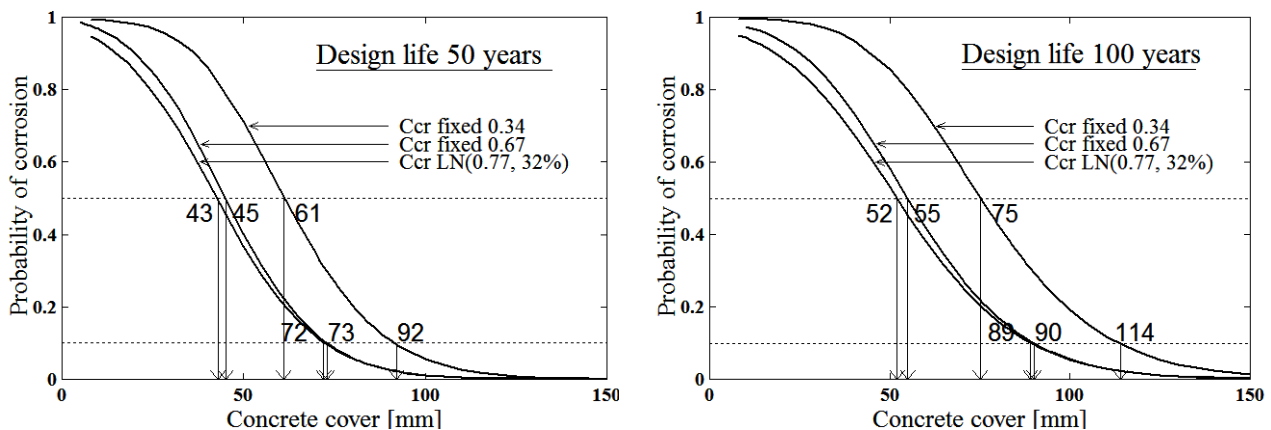
$$g(X) = C_{cr} - C(x, t)$$

where  $X$  is a vector of the statistical parameters as diffusion coefficient, surface chloride concentration, concrete cover etc.

Probabilistic calculations of required concrete cover for design service lives of 50 and 100 years, respectively, are performed. The chloride ingress is calculated based on Ficks' 2. law of diffusion, including the time dependency of the diffusion coefficient. The results are presented in Figure 3.

As seen, the lognormal distribution gives approximately the same results as using a characteristic value of  $C_{cr} = 0.67$  % by weight of cement. To illustrate the sensitivity of  $C_{cr}$  a conservative value of 0.34 is also included. For an acceptance limit (probability of corrosion initiation) of 10 % the cover thickness needed to obtain 50 years service life becomes 73 mm and 92 mm for  $C_{cr} = 0.67$  and 0.34, respectively. For a 100 year design service life the corresponding cover thickness becomes 90 mm and 114 mm respectively.

The sensitivity of the critical chloride content,  $C_{cr}$ , is clearly illustrated by the following observations: If a characteristic value  $C_{cr}$  of 0.67 is used, a concrete cover of about 90 mm results in a design service life of 100 years. However, if  $C_{cr}$  is reduced to 0.34 the service life is reduced to 50 years!



**Figure 3:** Effect of  $C_{cr}$  on required concrete cover for design service lives of 50 and 100 years, respectively ( $C_{cr}$  given in % weight of cement)

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1. Schiessl, P. and Raupach, M. (1992): "Monitoring system for the corrosion risk of steel in concrete structures", Concrete International V. 14, No. 7, July 1992, pp 52-55
2. Markeset, G.(2000): "Service Life Predictions of Marine Concrete Structures – Consequences of Uncertainties in Model parameters"; Proceedings, Nordic Mini Seminar: "Prediction Models for Chloride Ingress and Corrosion Initiation in Concrete Structures", Chalmers Institute of Technology, Gothenburg, Sweden, Publikation P-01:6
3. fib (2006): "Model Code for Service Life Design", Bulletin 34
4. Browne, R.D.(1982): "Design prediction of the life of reinforced concrete in marine and other chloride environments", Durability of Building Materials, Vol. 3, Elsevier Publishing
5. Larssen, R.M.(2001): "Parametervariasjon i levetidsmodeller for marine betongkonstruksjoner" (in Norwegian), Dr.Ing. A.Aas-Jakobsen AS, Oslo, Norway.

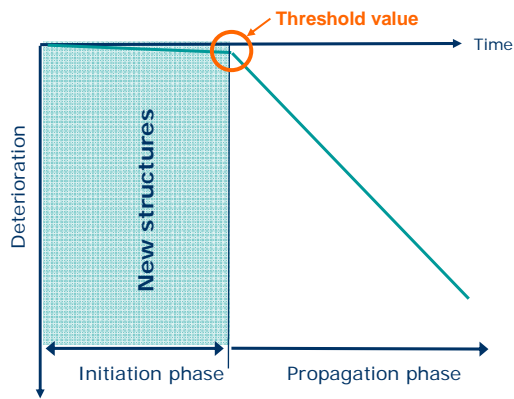


# Critical chloride content and its influence of service life predictions

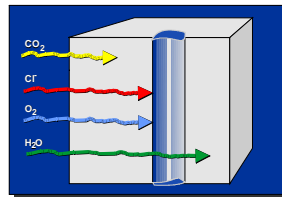


Gro Markeset, Dr. ing.  
Project Manager, COIN

# Deterioration and service life



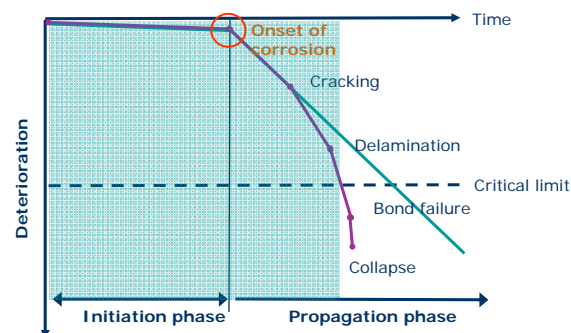
Tuutti's two phase model





## Chloride induced corrosion

- **Initiation phase:**
  - modelling of chloride ingress
- **Propagation phase:**
  - modelling of concrete/steel deterioration



## Definition of critical chloride content ( $C_{cr}$ )

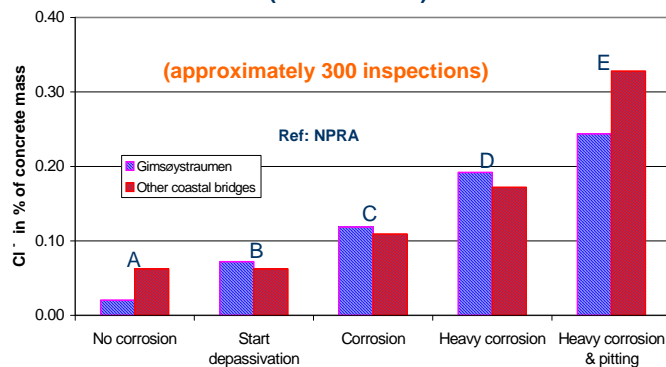
- $C_{cr}$  can be defined in two different ways:
  1. Chloride content required for *depassivation of the reinforcement surface*
  2. Chloride content associated with some *acceptable deterioration*
- From "*fib Model Code for Service Life Design, 2006*":
  - "The total chloride content which leads to the *depassivation of the reinforcement surface and initiation of iron dissolution*, irrespective of whether it leads to visible corrosion damage on the concrete surface".

## Experience from real structures

- Observed  $C_{cr}$  in real structures are often based on visual inspection of the reinforcement after chiselling, in combination with determined chloride content
- The evaluation of rebar corrosion are classified in corrosion levels:
  - A: No sign of corrosion
  - B: Signs indicting depassivation
  - C: Corrosion
  - D: Heavy corrosion
  - E: Severe corrosion, pitting etc.

## Bridge investigations

Chloride content (mean values) & corrosion level A-E



Example from Gimsøystraumen bridge:

B:  $C_{crit} = 0.07\%$  Cl<sup>-</sup> of concrete mass, variation coeff. 98%

C:  $C_{crit} = 0.12\%$  Cl<sup>-</sup> of concrete mass, variation coeff. 78%

Chloride content for onset of corrosion – is it B or C or?

## Investigation of $C_{cr}$ in existing structure using corrosion sensors

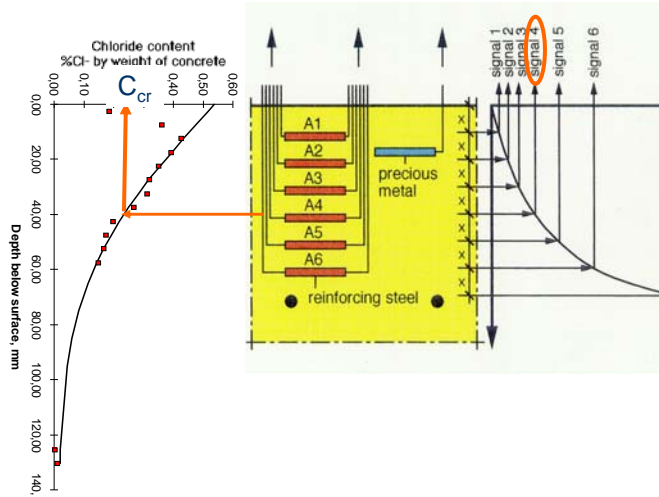
- Procedure
  1. Installation of corrosion sensors in existing structure to determine the depth of the critical chloride content
  2. Measurement of chloride profile from the cores drilled out where sensors have been installed
  3. Critical chloride content obtained by comparing the chloride profiles with the sensor reading at the depth of depassivation

## Corrosion sensors type “Expansion-Ring-Anode System” for non-submerged conditions

Ref: S+R Sensortec

- Consists of six measuring rings in different distances from the concrete surface, in 1 cm -steps from 1 to 6 cm.
- Ingress of chlorides and/or carbonation from the concrete surface into the concrete and the subsequent corrosion risk of the reinforcement can be measured
- As long as the critical chloride content have not reached the surface of the outer anode, all electrical currents are low.
- Limit values for activity (exceeding depassivation) of the single anodes under usual conditions:
  - Voltage between anode and cathode of about 400 mV
  - Electrical current of about 10  $\mu$ A

## Principle for the determination of $C_{cr}$



## Measuring of $C_{cr}$ in a Norwegian quay

- 14 corrosion sensors installed in a 37 years old concrete quay in the Northern part of Norway-
- Concrete properties
  - coarse-grained Portland cement
  - water/cement-ratio varying between 0.40 and 0.50.
- Chloride profiles determined on 50 mm cores extracted from the drilled holes for sensor installation



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## Installation of the corrosion sensors

a) Concrete surface in aggressive environment

b) Drilling of a hole  $\varnothing 30$  or  $\varnothing 56$  mm

c) Inserting of the Expansion Ring Anode

d) Expanding of the rings

e) Inserting the removable protection cap

f) Inserting plug during measurements

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## Conclusions from the corrosion sensor measurements

- The cored hole in which the sensor shall be placed should be extremely precise in alignment and in free diameter. A tolerance in diameter of  $\pm 0.5\text{mm}$  was specified.
  - the robustness and the general installation tolerances of the system should be increased
- Recordings from apparently undamaged sensors have shown considerable variations in individual readings seemingly without correlation between current flow, voltage and electric resistivity.
  - data interpretation needs additional user-oriented development and guidance

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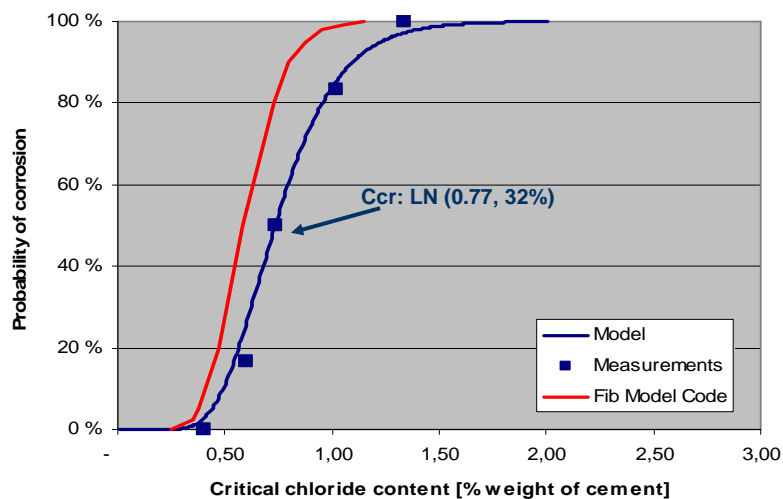
## Determination of $C_{cr}$

Due to the uncertainties and variations in the measurements the critical chloride content is considered in terms of probability or risk of corrosion.

Table: Results compared to Browne's corrosion risk classification

Probability/risk of corrosion	Norwegian Quay	Browne
Negligible	<0.4	<0.4
Possible	0.4-0.7	0.4 -1.0
Probable	0.7-1.3	1.0 – 2.0
Certain	>1.3	>2.0

## Statistical modelling of $C_{cr}$



Example from Gimsøystraumen bridge in Norway:

B: Mean  $C_{crit}$  = 0.46 % Cl<sup>-</sup> by weight of binder, variation coeff. 98%

C: Mean  $C_{crit}$  = 0.76 % Cl<sup>-</sup> by weight of binder, variation coeff. 78%

## Service life predictions

### Modelling of chloride ingress by Fick's 2. law of diffusion

$$C(x,t) = C_s \left( 1 - \operatorname{erf} \left[ \frac{x}{2\sqrt{D(t) \cdot t}} \right] \right)$$

$$D(t) = D_0 \quad \text{constant diffusion}$$

$$D(t) = D_0 \left( \frac{t_0}{t} \right)^\alpha \quad \text{time dependant diffusion}$$

where t: Exposure period  
 x: Distance from exposed surface  
 C<sub>s</sub>: Chloride surface concentration  
 D(t): Chloride diffusion coefficient at time t  
 D<sub>0</sub>: Chloride diffusion coefficient determined at t=t<sub>0</sub>  
 t<sub>0</sub>: Reference period  
 α: Age factor

Corrosion initiation:  $C(c,t) \geq C_{cr}$

c: Concrete cover  
 C<sub>cr</sub>: Critical chloride content (threshold value)

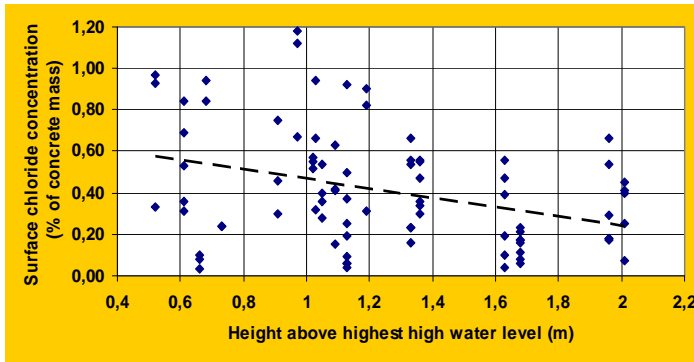
## Fick's 2. law of diffusion

### Deterministic vs. probabilistic

- **Deterministic analyses:**
  - Parameters given as unique values, e.g. the mean value.
  - Each set of parameters give a service life for a given accept limit of the chloride concentration
- **Probabilistic analyses:**
  - Variation of parameters described by mean values and standard deviations and distributions.
  - Each set of parameters give a service life and a probability for exceeding the given accept limit of the chloride concentration

$$g(\mathbf{X}) = C_{cr} - C(x,t)$$

## Surface chloride concentration obtained on Norwegian quay slabs



## Service life calculations – An Example

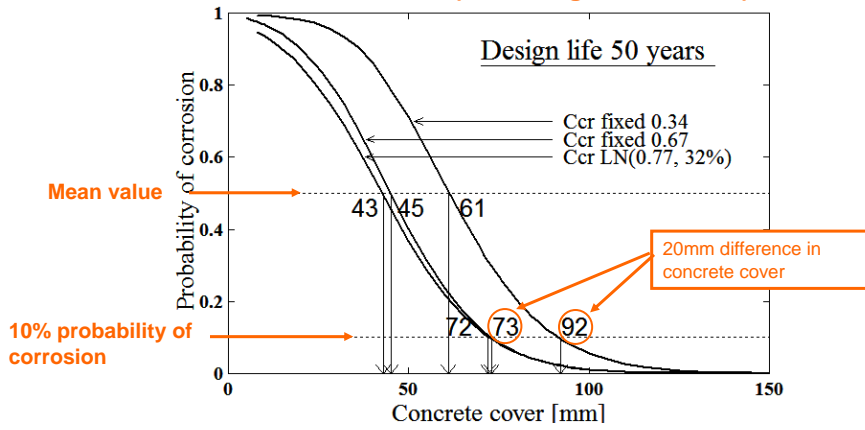
### input parameters and distributions:

- Chloride concentration on concrete surface,  $C_s$   
 $C_s = \text{LN}(2.67, 60\%)$  (% of cement mass)
- Cover thickness,  $x$   
 $x = \text{LN}(x, 10)$  [mm]
- Chloride diffusion coefficient,  $D_0$   
 $D_0 = \text{LN}(7.0 \cdot 10^{-12}, 30\%)$  [ $\text{m}^2/\text{s}$ ]
- Ageing factor,  $\alpha$   
 $\alpha = \text{N}(0.4, 15\%)$
- Critical chloride concentration,  $C_{cr}$   
 $C_{cr}: \text{LN}(0.77, 32\%)$   
Characteristic values:  $C_{cr} = 0.34$  and  $0.67$  (% of cement mass)
- Acceptance criterion for corrosion initiation:  
10 % probability of corrosion (SLS)



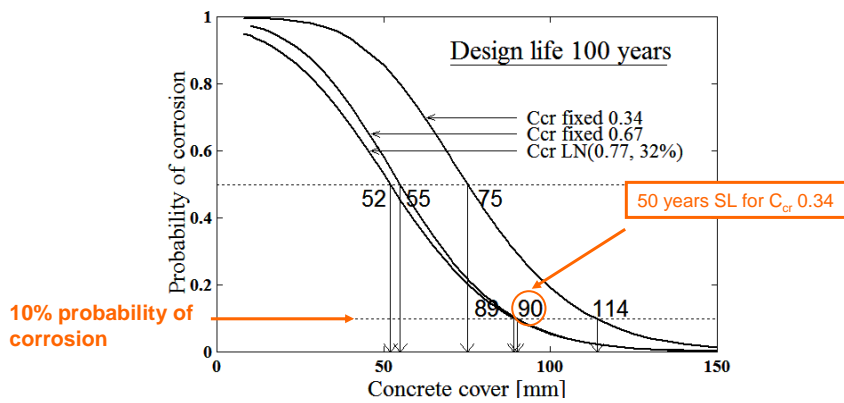
## Reliability based service life predictions - Example: design life 50 years

Effect of  $C_{cr}$  (% of weight of cement)



## Reliability based service life predictions - Example: design life 100 years

Effect of  $C_{cr}$  (% of weight of cement)



## Concluding remarks

- The calculated service life are very sensitivity to the critical chloride content as illustrated;
  - for the same cover thickness, the service life is 50 years for a characteristic value of  $C_{cr} = 0.34\%$  and 100 years for  $C_{cr}=0.67\%$  (by weighth of cement).
- The definition of  $C_{cr}$  is decisive in order to know how much of the “propagation phase” that are included in the limit state named “onset of corrosion”.

**$C_{cr}$  is a parameter needing much more attention than recognized in the service life predictions!**



## **10 A field study of critical chloride content**

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### **“A field study of critical chloride content in reinforced concrete with blended binder”**

*Luping Tang*

*CBI and Chalmers University of Technology*



## A Field Study of Critical Chloride Content in Reinforced Concrete with Blended Binder

TANG, Luping<sup>1,2</sup> and UTGENANNT, Peter<sup>1</sup>

<sup>1</sup> CBI Swedish Cement and Concrete Research Institute, Borås, Sweden

<sup>2</sup> Chalmers University of Technology, Gothenburg, Sweden

### Extended Abstract

In the beginning of 1990's over 40 reinforced concrete slabs with different types of binder and water-binder ratios were exposed in a marine environment at Swedish west coast. After over 13 years' exposure, the conditions of steel bars in the concrete slabs were investigated using both non-destructive and destructive methods. This paper presents the results from the investigation.

The field site is situated in the Träslövsläge harbour in the south western part of Sweden, 80 km south of Gothenburg. At the field site the average annual temperature in the air is about 11 °C and the average chloride concentration in the seawater is about 14 g/l. The test specimens are slabs (height 100 cm, width 70 cm, thickness 10-20 cm). Three steel bars, one smooth stainless and two ribbed carbon steel, were embedded in each slab with covers between 10-30 mm in most cases and 35-55 mm in some cases. Half of the slab was exposed under the seawater and another half to the air.

A newly developed rapid technique, RapiCor [1,2], was used for non-destructive measurement of corrosion. Based on the results from the non-destructive measurement, the actual corrosion of steel bars in five concrete slabs was visually examined and the chloride profiles in the penetrating direction as well as at the cover level were measured. The information about these five slabs is listed in Table 1.

Table 1: Concrete slabs taken from Träslövsläge for the laboratory investigation

Binder type	Binder kg/m <sup>3</sup>	Water- binder ratio	Air content %	Compr. strength MPa, 28d	Rebar diam. mm	Cover mm Bar 1/2
100% Anl	450	0.35	6.0	70	20	20/15
90% Anl+10%SF	420	0.40	6.6	65	12	15/15
100% Anl	420	0.40	2.1	79	12	10/15
78.5%DK+17%FA+ 4.5%SF	420	0.40	6.1	69	12	15/10
80% Anl+20%FA	616	0.30	3.0	98	12	15/10

These five slabs were taken from the field site to the laboratory, where the non-destructive corrosion measurements were carried out again in a small grid in order to identify the active corrosion positions. Afterwards a groove along each rebar was cut from the back of the slab, so as to facilitate the release of rebar for visual examination. After release of rebar, concrete samples were taken at the depth where the rebar was embedded and at the positions where the corrosion was measured by the RapiCor technique. The acid soluble chloride and calcium content in each sample were determined by titration.

Based on the visual examination of the steel bars from the five selected slabs, it has been verified that the non-destructive RapiCor technique gives satisfactory estimation of corrosion. Therefore, this technique was used for non-destructive measurement on the rest of slabs exposed in the Träslövsläge field site.

Relationships between corrosion rate and chloride content are shown in Figure 1. From the results it can be seen that, the criterion for actual high corrosion ( $10 \mu\text{m}/\text{year}$ ) are always related to chloride content about 1% by mass of binder, despite of the types of binder. It is understandable that high chloride content may not necessarily mean high corrosion rate, but high corrosion rate should be caused by higher chloride content with regard to chloride-induced corrosion.

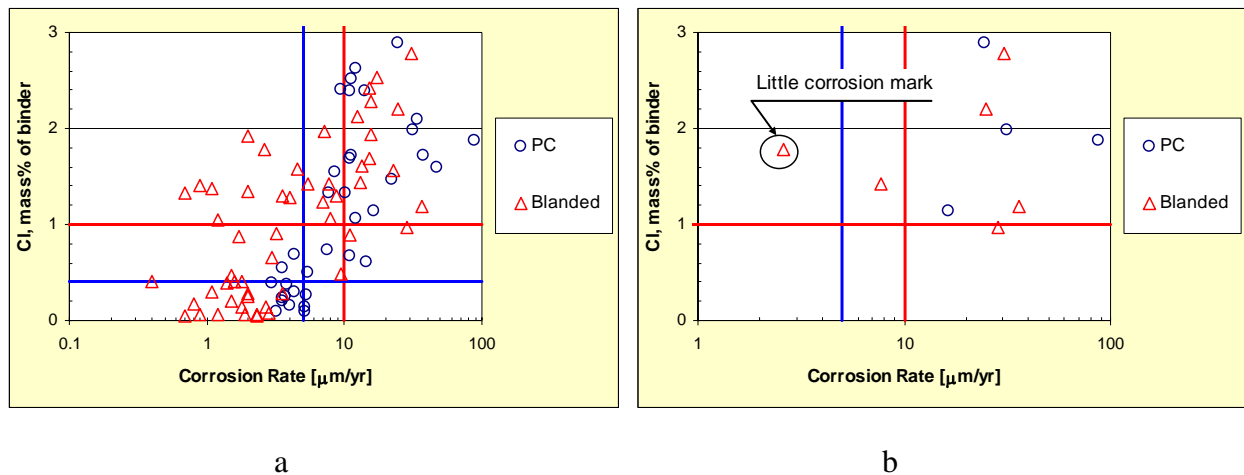


Figure 1: Relationships between corrosion parameters and chloride content exposed in the field, a – all the data, and b – data with active corrosion measured by the RapiCor and observed by visual examination.

Since the corrosion measurement is for the instantaneous status, the actual initiation of corrosion is unknown from this study. Therefore, the chloride level 1% by mass of binder may not be the same as the conventionally defined threshold value, but can be taken as the critical level for significant on-going corrosion that is visible by destructive visual examination.

In the literature, it is believed that critical chloride content in the concrete with blended binder should be lower than that in the OPC concrete due to lower alkalinity in the pore solution with blended binder [3,4]. The results from this field study do not show this tendency. Since the pore structures in the concrete with blended binder are normally finer than those in the OPC concrete, these finer pore structures may prevent the reinforcement from depassivation. Therefore, the factor of pore structures should also be taken into account when defining “critical chloride content” for initiation of reinforcement corrosion in concrete.

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- [1] Tang L., “Mapping Corrosion of Steel in Reinforced Concrete Structures”, SP RAPPORT 2002:32, SP Sveriges Provnings- och Forskningsinstitut, Borås, 2002.
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## **11 Reference material for calibrating chloride analysis**

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### **“Reference material for calibrating chloride analysis of hardened concrete”**

*John B. Miller*

*Millab Consult A.S.*





## Reference Material for Calibrating Chloride Analysis of Hardened Concrete

John B. Miller, (Millab Consult A.S., Oslo, Norway)

### 1. Introduction

When analysing, it is important to calibrate against relevant materials containing known amounts of the substance to be determined, otherwise it is difficult to know whether a particular analytical method is returning correct results. In simple cases, standardised solutions containing precisely weighed-in amounts of pure substances can be used for, for example, titration calibration. In more difficult cases, such as that of determining chloride content in concrete, the task of producing a reference material for calibration is much more complex and onerous. The creation of concrete reference material containing precisely known amount of chloride, though simple in principle, is in fact a demanding and expensive operation.

Reference materials with two different water contents and 6 different chloride contents, have been produced [1,2], and have been used to conduct two, previously published, independent Round-Robin tests, the results of which demonstrated very clearly the large discrepancies that can occur between methods and laboratories, when analysing identical material. In these tests, results deviating by more than 100% from the true values were returned [3]. Other parties have found similar results [5].

### 2. Preliminary Considerations

The analysis of hardened concrete for total chloride content entails three main operations, assuming that representative concrete samples have been obtained in the first place. These operations are:

- the reduction of the material to a fineness that allows easy dissolution
- the dissolution of the material in acid
- the analysis proper

In the laboratory, hardened concrete can be reduced using crushers, grinders and mills to a fineness that is convenient for dissolution in acids, thus freeing the chloride to solution. In the field, the majority of samples are taken by the collection of the tailings produced by 16 to 22 mm hammer drilling, which produces a particulate material that is much coarser than laboratory reduced material, and where complete acid dissolution needs greater care. With both types of material, it is essential that the chloride extraction is complete, and thus the grain size distribution of the calibration material must resemble that of samples commonly taken by hammer drilling.

Many analytical methods exist, ranging from common volumetric or potentiometric titration, to methods using proprietary equipment such as Quantab, RCD, and RCT. It is the author's contention that the actual method used is of little or no importance providing correct results are returned for known material.

### 3. Production of precisely known reference material.

In order to produce materials that are dependable, the following factors need to be controlled and/or known:

- Chloride content of raw materials (water, sand, gravel, cement and any additives used)
- Content of the raw materials (sand, gravel, cement)
- Cleanliness of the equipment and machinery used for mixing
- Exact weights of weighed in materials and amount of mixing water
- Addition of precisely known amounts of chloride to produce a range of chloride contents
- Proper hardening of the concrete bodies produced
- Drying of the bodies to constant weight
- Crushing and grinding of the concrete to the correct grain-size distribution
- Homogenisation of the reduced material
- Hermetically packing the reduced materials in suitable amounts (10 g per package)

- Withdrawal of sufficient numbers of randomly selected sample packs for chloride analysis
- Statistical treatment of the results in order to estimate standard deviation and deviation from the mean of the chloride contents of the sample packs.
- Production of enough material to supply the world community for upwards of 30 years

Since samples are commonly taken in the field by hammer drilling, the first step was to collect sufficient material from various types of hammer drill to allow grain size distribution curves to be made. These curves were then used to examine crushing and grinding methods that could produce material having a distribution close to the average of the drilled materials. This is important, especially when using commercial methods such as the Rapid Chloride Test (RCT) or Rapid Chloride Determination (RCD), since the extraction technique must be able to completely disband cemented particles. To find such a method entails sending blocks of concrete to various laboratories to identify one that could produce such material. We found one such laboratory – Taylor Engineering Laboratory, London, UK.

### **3.1 Preparation of mixing equipment and constituent materials.**

Thus ensured that it was possible to produce material with the required grain size, the next step was to produce suitable batches of concrete. To do this, all materials were first homogenised in excess of required quantities, and samples removed by quartering for chloride analysis using classic potentiometric titration of acid extracts. The materials, including the cement, were then dried to constant weight at 105°C, and thereafter kept in airtight containers until use.

To avoid contamination, all mixing equipment was either carefully cleaned of all previous residues, or new equipment was used depending on the cost of the needed items. Water used for final rinsing, and for mixing the concrete batches, was distilled water.

### **3.2 Precautions**

During crushing and grinding, any dust produced had to be collected and returned to the material since it was not known whether the dust contains more or less chloride than the main material. This required some adaptation of the equipment used.

To protect the material from weight changes that could result from moisture exposure or carbonation, it was necessary to pack the material in hermetically sealed containers. We used the same type of sachet as used for packaging shampoos, liquid soaps, wet tissues and the like, such as are found in hotel rooms or used by airlines. These are made from plastic coated aluminium foil, and are sealed by welding. The packing machine used had equipment for collecting dust released at the hopper and doser, and this was later analysed for chloride enrichment, since it was feared this could disturb the chloride content of the material being packed. However, no such enrichment was found.

### **3.3 Statistical sampling and determination of standard deviations from true chloride content**

During packing, the packages issuing from the machine were sampled statistically in accordance with a random number generator. The contents of these sachets were then analysed and the results used to calculate the standard deviation of the various chloride contents of each of the 12 batches of concrete [4]. The results compiled in the table show that the produced material is entirely suitable for the calibration of analytical methods of chloride analysis in hardened.

## **4. Nordic and Dutch Round Robin Tests**

The reference material was used in a previously reported Round Robin (3) test to evaluate three chloride analysis techniques commonly used in Norway for accuracy, precision and reproducibility. This programme was funded by NORTEST, a Nordic body within the field of technical testing and measurements, and five Nordic laboratories participated. The chloride analysis techniques selected were the Quantab Test, Chloride Selective Electrode Potentiometry and Volhard Titration. The reported results were summarised and discussed for each of the chloride analysis techniques separately, and are presented in tables showing the mean values of the four parallels, the standard deviations of the means and deviations in % of the nominal values. Deviations were very large for all 4 methods.

Conflicting results of chloride analysis have also been experienced by the Civil Engineering Division of the Ministry of Transport, Public Works and Water Management in Holland. The Civil Engineering Division, therefore, had concrete reference material, with both Portland cement and blast furnace slag cement, produced in order to examine the reliability of chloride analysis [5]. A total of 17 Dutch laboratories received nine sachets of reference concrete samples and were asked to perform chloride analysis in duplicate, according to their standard procedure, and to report the results as chloride content by weight of cement. None of the laboratories knew that the results were to be used in a Round Robin test. Ten of the laboratories used Volhard Titration, one used Mohr Titration, while Chloride Selective Electrode Potentiometry, Potentiometric Titration and Spectrophotometry were used by two laboratories. The results of this test also showed unacceptably large variations, thus confirming the necessity of calibration against known material.

#### Reference materials, their chloride contents & standard deviations

Target Cl content	w/c	True Cl content in % w/w of		Standard deviation**	Added as
		Concrete	Cement		
0.0000	0.58	0.006	0.051	$1.5 \times 10^{-3}$	NaCl
0.0250	0.58	0.028	0.236	$1.6 \times 10^{-3}$	NaCl
0.0500	0.58	0.056	0.472	$1.9 \times 10^{-3}$	NaCl
0.1000	0.58	0.097	0.818	$4.5 \times 10^{-3}$	NaCl
0.2000	0.58	0.192	1.619	$4.4 \times 10^{-3}$	NaCl
0.5000	0.58	0.468	3.947	$8.3 \times 10^{-3}$	NaCl
0.1000	0.58	0.097	0.818	$2.3 \times 10^{-3}$	CaCl <sub>2</sub>
0.0000	0.45	0.004	0.034	$7.2 \times 10^{-4}$	NaCl
0.0250	0.45	0.028	0.236	$1.6 \times 10^{-3}$	NaCl
0.0500	0.45	0.050	0.422	$1.0 \times 10^{-4}$	NaCl
0.1000	0.45	0.094	0.793	$1.7 \times 10^{-3}$	NaCl
0.2000	0.45	0.187	1.577	$2.4 \times 10^{-3}$	NaCl
0.5000	0.45	0.451	3.803	$3.9 \times 10^{-3}$	NaCl
0.1000	0.45	0.095	0.801	$1.8 \times 10^{-3}$	CaCl <sub>2</sub>
** Of chloride content in sachet					

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1. Gran H.C and Farstad, T: "Production of reference concrete with known chloride contents" Project no. 02877, Norwegian Building Research Institute, Oslo, Norway, 1990.
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4. Gran, H. C. "Measurement of chlorides in concrete - an evaluation of three different analysis techniques" NBI Project Report 110 -1992, Oslo, Norway 1992.
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## **12 On the need for more precise thresholds values**

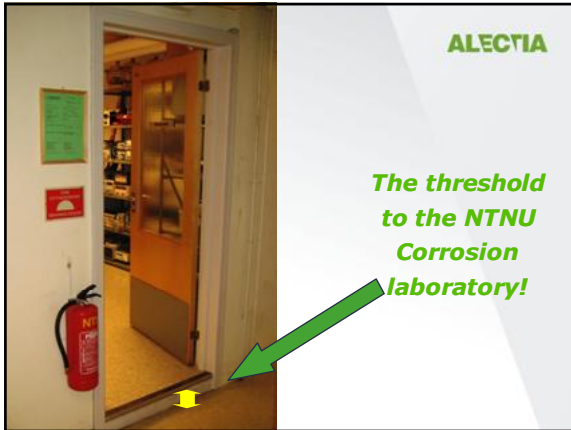
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**“On the need for more precise threshold values for chloride initiated corrosion in design, repair and maintenance of reinforced concrete structures – a consultant’s view”**

*Jens Mejer Fredriksen*

*ALECTIA A/S*





**ALECTIA**

*On the need for more precise threshold values for chloride initiated corrosion*

- ▀ in design
- ▀ repair
- ▀ maintenance

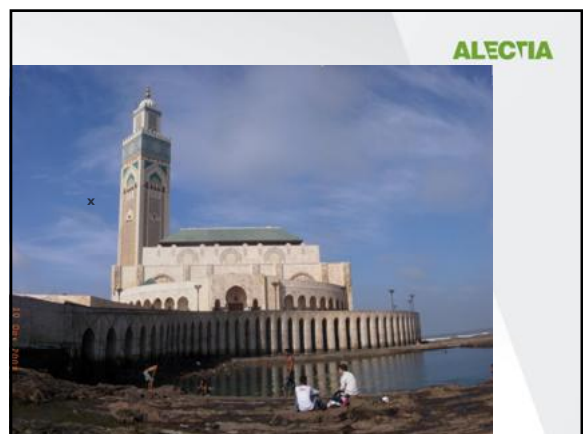
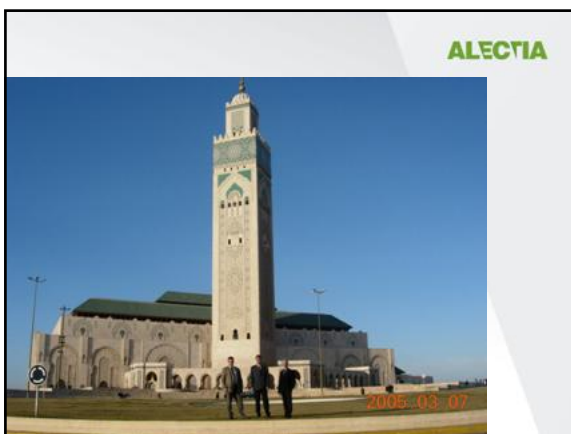
*of reinforced concrete structures*  
- a consultant's view

**Jens Mejer Frederiksen**  
[jmf@alectia.com](mailto:jmf@alectia.com), ALECTIA A/S, Denmark

**"Service life prediction" is in many cases closely related to "Prediction of time to corrosion initiation"**

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<p><b>The Great Belt Link</b> Constructed 1987-1998 Requirement 100 years</p>	<p><b>Mosquée Hassan II, Casablanca</b> (Constructed: 1987-1993) No requirements! Repaired (!): 2005-2008</p>
<p><b>New Port Tanger Med. I</b> Constructed 2004-2007 Requirement 100 years</p>	





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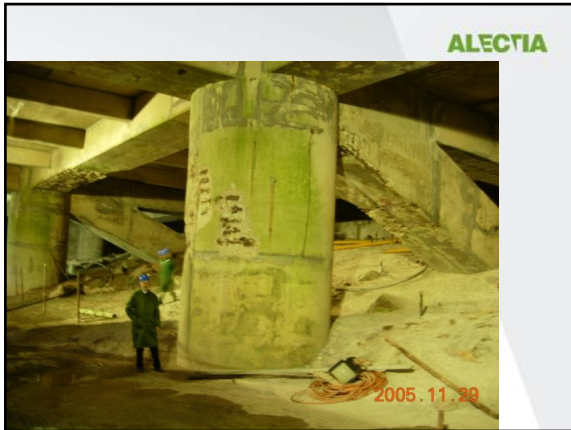


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**“Service life prediction”**

**What do we really want?**

- A widely accepted and strictly logical model/ system to take us through durability design for concrete structures in saline environments

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**“Service life design etc.”**

**Including guidelines for:**

- Design
- Specifications
- Tender documents
- Contract
- Concrete manufacturing
- Construction and concreting
- Commissioning

**...and may be even:**

- Operation
- Maintenance
- Repair

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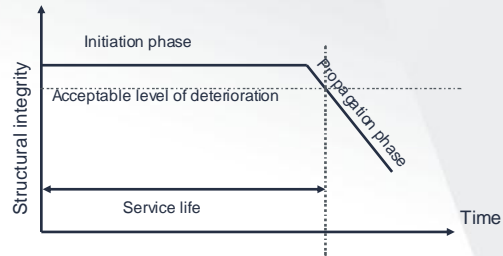
**...we do however not have such a model or system today!**

- What we have is a part of a framework
- It is neither strictly logical nor widely accepted
- It does not give us clear information on how to make specifications
- It is based on both short time experience and on expert opinions!

...but we might be able to reach our goal in a (4-8 years) time

- When we have a widely accepted ingress model we will be focusing on the soft spots
- We already know – and we have known it for many years – that we need to understand the corrosion initiation process
- If we do not understand it we can not make sensible service predictions and hence we will not reach our goal.

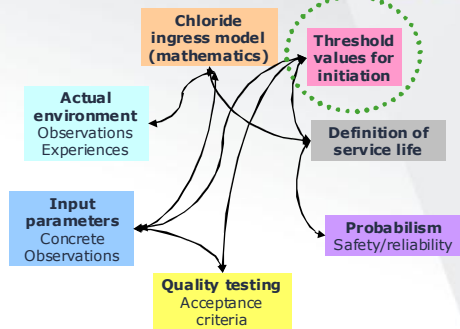
Service life definitions



Service life – or technical service life

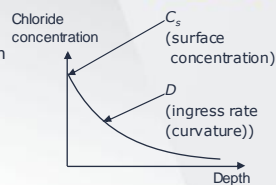
- Almost anything can be maintained to have a service life of 100 years or more
- It is almost just a matter of maintenance and costs
- Sometimes maintenance is however so costly and annoying that we rather demolish and reconstruct
- This is why we are asked by the owners to predict service life!

“Service life prediction” - many interconnected disciplines



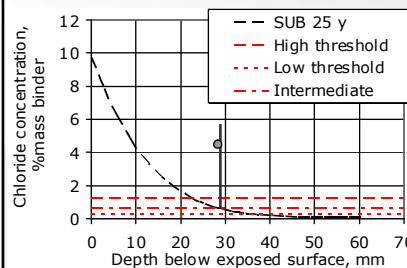
Chloride ingress

- Chloride penetrates through the concrete surface and build up a profile in the concrete cover with a characteristic shape →
- The chloride profile at any time can be fitted by the error function solution to Fick's 2<sup>nd</sup> law the described by the parameters  $C_s$  and  $D$ :



$$C(x,t) = C_s - (C_s - C_i) \operatorname{erf} \left( \frac{x}{2\sqrt{t \times D}} \right)$$

Chloride profile



- The chloride profile is used to evaluate the risk for reinforcement corrosion
- The threshold value is an important parameter in this evaluation
- The value still has to be chosen by estimates

## Chloride ingress

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- Ingress of the position of the critical chloride concentration,  $x_{cr}$  can be estimated by:

$$x_{cr} = K\sqrt{t}$$

- $C_s$ ,  $C_{cr}$  and  $D$  are parameters in the penetration parameter  $K$ :

$$K = 2\sqrt{D} \operatorname{erf}^{-1} \left( \frac{C_s - C_{cr}}{C_s - C_i} \right)$$

## The parameters

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### The $D$ value

- We can control the value of  $D$  by choice of concrete composition
- The environment influences the value of  $D$

### The $C_s$ value

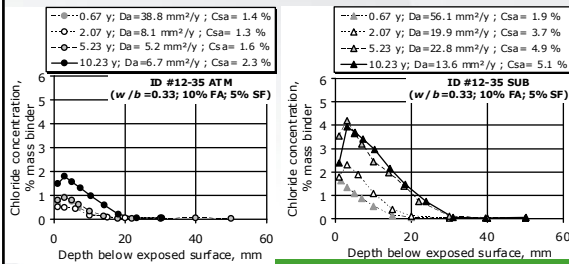
- The environment controls the value of  $C_s$
- We can influence the  $C_s$  value by choice of concrete composition

### The $C_{cr}$ value

- We can control the  $C_{cr}$  value by choice of concrete composition
- The environment influences the value of  $C_{cr}$

*I.e.: We can control both  $D$  and  $C_{cr}$  !*

## Measured chloride profiles, Träslövsläge ALECTIA

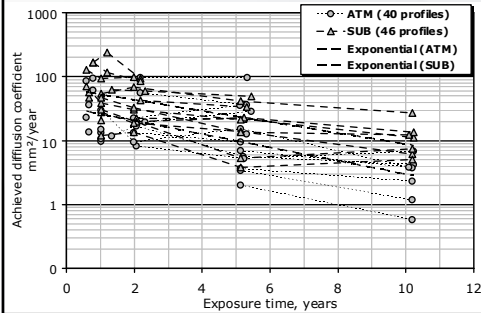


*$D_a$  is decreasing and  $C_{sa}$  is increasing!*

*We do not know why, but anyhow we can model the result of both!*

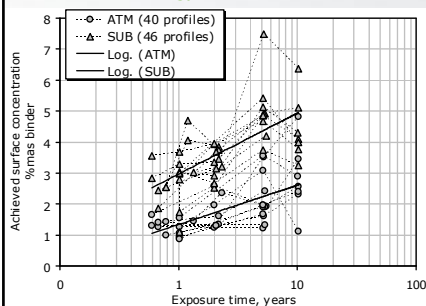
## Fitted parameters from chloride profiles $D_a$ is decreasing

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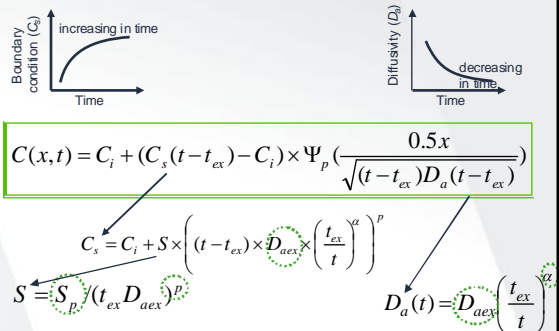
## Fitted parameters from chloride profiles $C_{sa}$ is increasing

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## The Mejlbro-Poulsen Model is the complete solution to Fick's 2<sup>nd</sup> law – it has four parameters

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**The Mejlbro-Poulsen Model has four parameters**

- $D_{aex}$
  - $\alpha$
  - $S_p$
  - $p$
- They can be found by conversion formulas when the following four parameters are known:
- >  $D_1$
  - >  $D_{100}$
  - >  $C_1$
  - >  $C_{100}$

Conversion formulas

$$\theta = \frac{1}{2} \times \log_{10} \left( \frac{1}{t_{ex}} \right) \quad D_{aex} = D_1 \times \left( \frac{D_1}{D_{100}} \right)^\theta$$

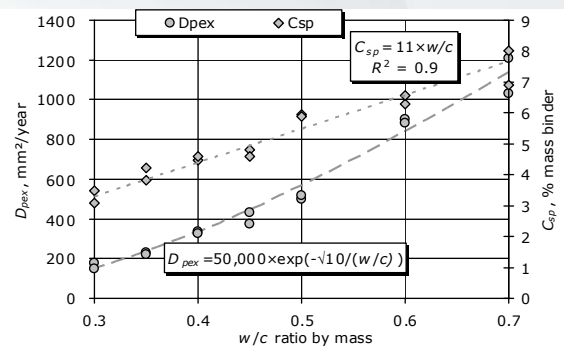
$$p = \frac{\log_{10}(C_{100}/C_1)}{\log_{10} \left( \frac{100-t_{ex}}{1-t_{ex}} \times \frac{D_{100}}{D_1} \right)} \quad S_p = C_1 \times \left( \left( \frac{D_1}{D_{100}} \right)^\theta \times \frac{t_{ex}}{1-t_{ex}} \right)^p$$

But how do we find

- >  $D_1$
- >  $D_{100}$
- >  $C_1$
- >  $C_{100}$

...we got the ideas from laboratory experiments...

**Laboratory tests, NT BUILD 443  
Plain concrete CEMI,  $0.3 \leq w/c \leq 0.7$ ,  
Paste volume 27 %**



Therefore the basic formulas are suggested to have the form:

$$C_1 = (11/A) \times \text{eqv}(w/c)_b \times k_{C1,env} \text{ [% mass binder]}$$

$$D_1 = B \times 6250 \times \exp \left( - \sqrt{\frac{10}{\text{eqv}(w/c)_D}} \right) \times k_{D1,env} \text{ [mm}^2\text{/year]}$$

$$\text{eqv}(w/c)_{\text{property } X} = \frac{w}{C + k_{FA, \text{property } X} FA + k_{MS, \text{property } X} MS}$$

The basic extrapolation formulas are suggested to be:

$$C_{100} = C_1 \times k_{C100,env} \text{ [% mass binder]}$$

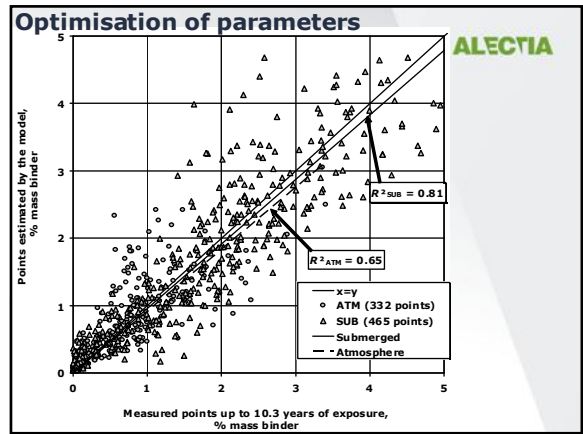
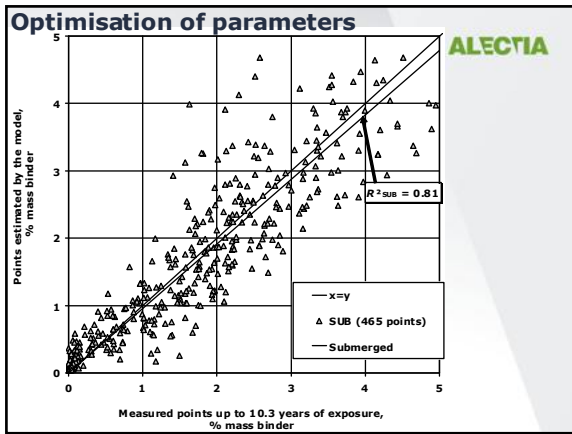
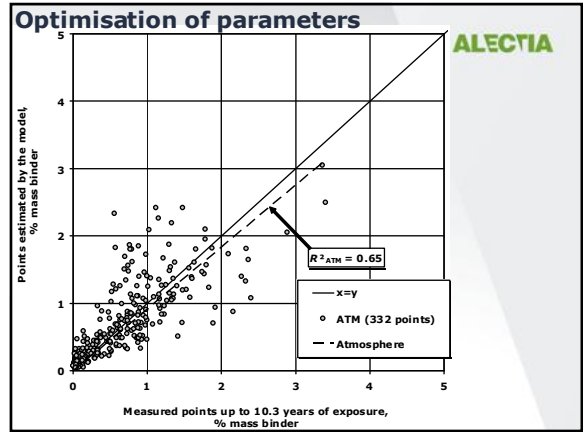
$$\alpha = (U \times \text{eqv}(w/c)_D + V) \times k_{\alpha,env}$$

$$D_{100} = D_1 \left( \frac{1}{100} \right)^\alpha$$

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### A 16 parameter system

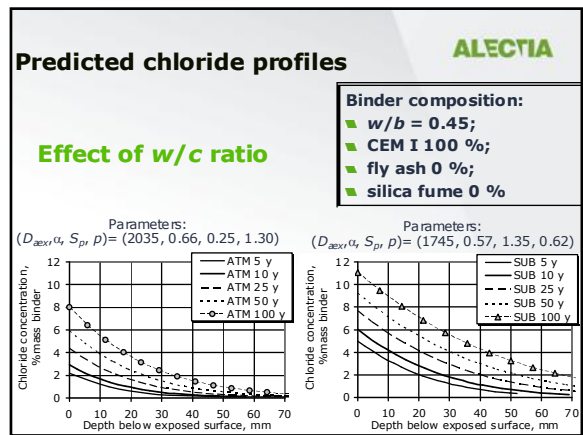
	Coefficient			Coefficient	
Parameters	$B$		Surface concentration	$k_{C1,env}$	atm
	$A$			$k_{C1,env}$	sub
	$U$			$k_{C100,env}$	atm
	$V$			$k_{C100,env}$	sub
Diffusion-coefficients	$k_{D1,env}$	atm	Efficiency factors, transport	$k_{FA}$	
	$k_{D1,env}$	sub		$k_{MS}$	
	$k_{i,env}$	atm	Efficiency factors, binding	$k_{FA}$	
	$k_{i,env}$	sub		$k_{MC}$	

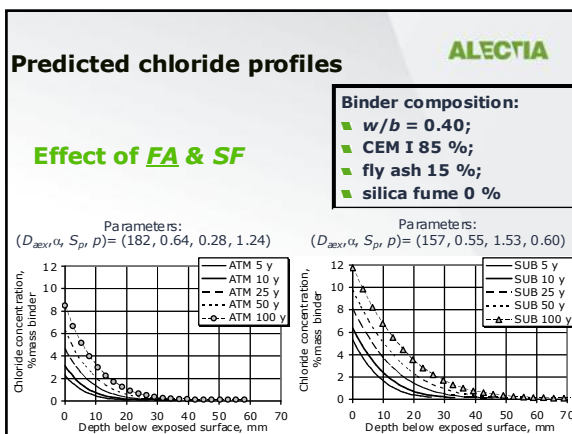
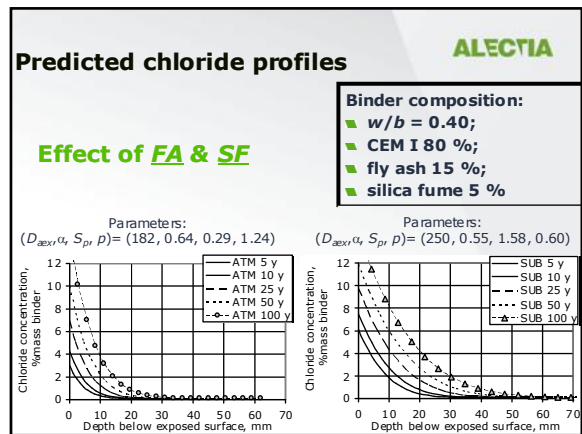
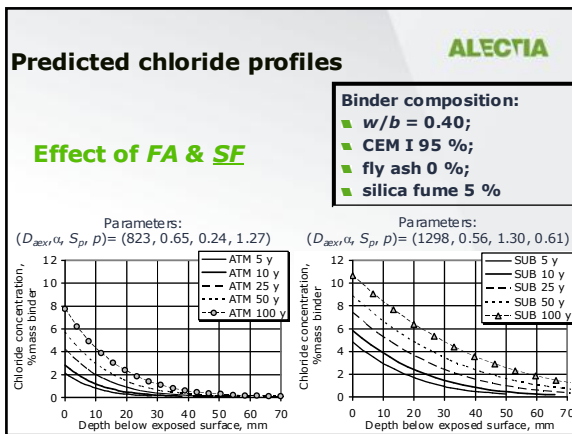
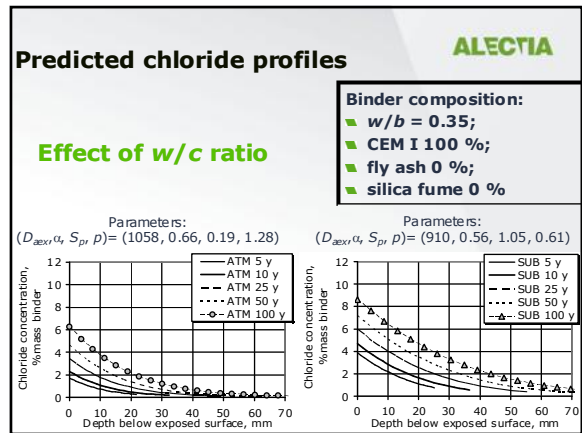
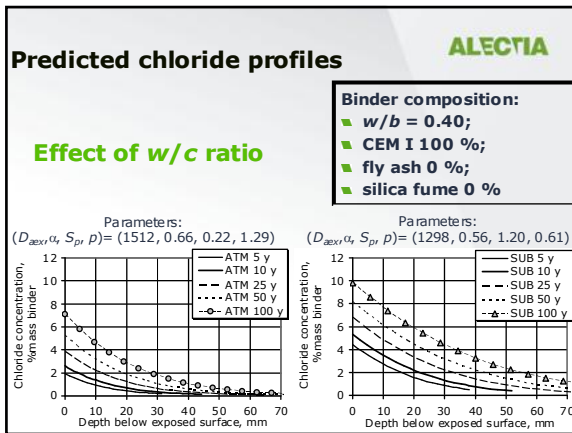


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### Derived design parameters

	Coefficient	Value		Coefficient	Value
Parameters	$B$	7	Surface concentration	$k_{C1,env}$	atm 0.6
	$A$	3		$k_{C1,env}$	sub 1.9
	$U$	0.1		$k_{C100,env}$	atm 8
	$V$	0.9		$k_{C100,env}$	sub 3.5
Diffusion-coefficients	$k_{D1,env}$	atm 0.6	Efficiency factors, transport	$k_{FA}$	6
	$k_{D1,env}$	sub 0.7		$k_{MS}$	1
	$k_{i,env}$	atm 0.7	Efficiency factors, binding	$k_{FA}$	-0.1
	$k_{i,env}$	sub 0.6		$k_{MC}$	-0.6





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**Chloride ingress modelling is on the threshold to succeed!**

- We can produce data that corresponds with our experience and intuition
- We need to verify the models on real structures
- We are still lacking good data

**...but what about chloride threshold values?**

**ALECTIA**

**HETEK-1**  
**– AEC, CTH, CEMENTA**

- Our scope was to make a complete framework
- We did not promise that it would not need verification – but it would be complete
- ...and it is!

■ Paul Sandberg delivered the threshold values for design!

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**Evaluation of published chloride threshold levels**  
**Advantages / disadvantages**

- **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.**
- **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.**
- **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.**
- **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.**

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

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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	Eisener & Böhm [1986]
0.3 - 0.7			Field	Henriksen [1993]
0.4			Outdoors	Bamforth & Chapman-Andrews [1994]
0.4 - 1.6			Laboratory	Hansson & Sørensen [1990]
0.5 - 2			Laboratory	Schiessl & Raupach [1990]
0.5			Outdoors	Thomas et al. [1990]
0.5 - 1.4			Laboratory	Tuutti [1993]
0.6			Laboratory	Locke & Siman [1980]
1.6 - 2.5		3 - 20	Laboratory	Lambert et al. [1991]
1.8 - 2.2			Field	Lukas [1985]
	0.14-1.8	2.5 - 6	Laboratory	Pettersson [1993]
		0.26 - 0.8	Laboratory	Goni & Andrade [1990]
		0.3	Laboratory	Diamond [1986]
		0.6	Laboratory	Hausmann [1967]
		1 - 40	Laboratory	Yonezawa et al. [1988]

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**Suggested design values for chloride threshold levels (black steel) in various Nordic exposure zones, [Paul Sandberg 1997, HETEK report 83]**

- Chloride threshold levels vary extensively in field exposed concrete, 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.

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

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Type of binder (PO = cement + puzzolanas)	Submerged zone	Marine/de-icing atmosphere + Marine splash zone	De-icing salt splash zone
	C <sub>cr</sub> %Cl of PO	C <sub>cr</sub> %Cl of PO	C <sub>cr</sub> %Cl of PO
<b>w/b 0.50</b>			
100 % CEM I	1.5	0.6	0.4
5 % SF	1.0	0.4	0.3
10 % SF	0.6	0.2	0.2
20 % FA	0.7	0.3	0.2
<b>w/b 0.40</b>			
100 % CEM I	2.0	0.8	0.6
5 % SF	1.5	0.5	0.4
10 % SF	1.0	0.3	0.2
20 % FA	1.2	0.4	0.3
<b>w/b 0.30</b>			
100% CEM I	2.2	1.0	0.8
5% SF	1.6	0.6	0.5
10% SF	1.2	0.4	0.3
20 % FA	1.4	0.5	0.4

**From the table created by Sandberg an approximating formula was made:**

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

The constant  $k_{cr, env}$  for the **road environment**.

Environment:	Wet Road environment	Dry Road environment	Distant Road Atmosphere (DRA)
Constant:	Splash (WRS)	Splash (DRS)	
$k_{cr, env}$	1	0.8	0.8

The constant  $k_{cr, env}$  for the **marine environment**.

Environment:	Submerged marine environment (SUB)	Marine environment Splash (SPL)	Marine Atmosph. (ATM)
Constant:			
$k_{cr, env}$	0.3	0.8	0.8



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

The activity factors for corrosion initiation to be used when calculating the  $eqv(w/c)_{cr}$  ratio:

Activity factor	Silica fume	Fly ash
$k$	-4.7	-1.4

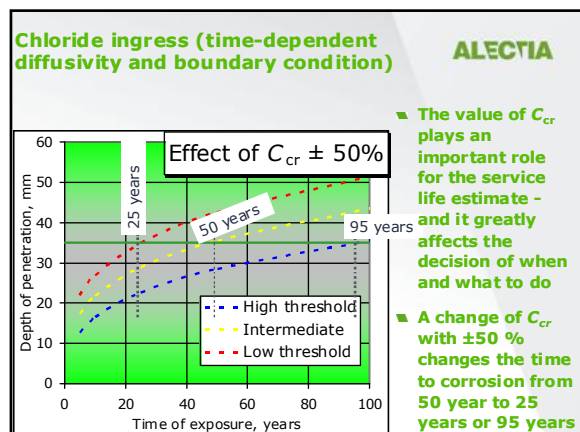
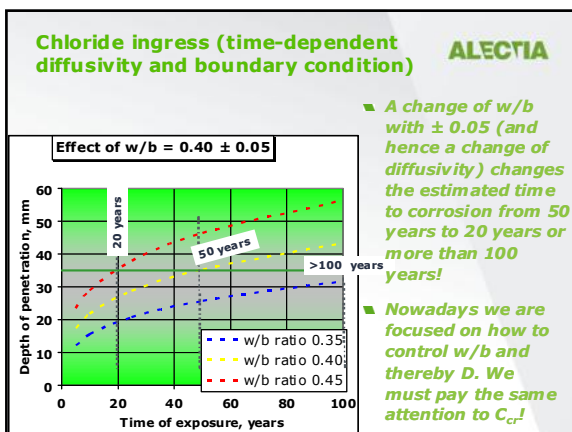
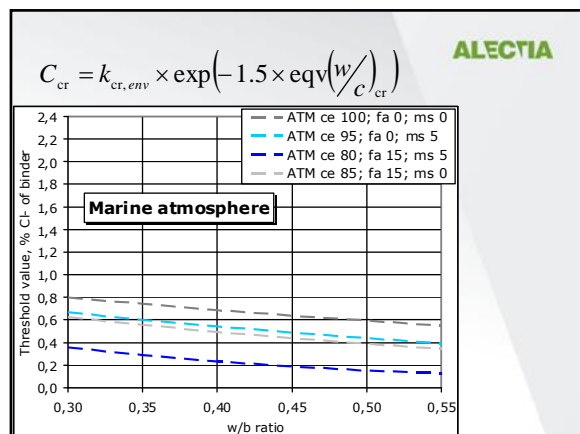
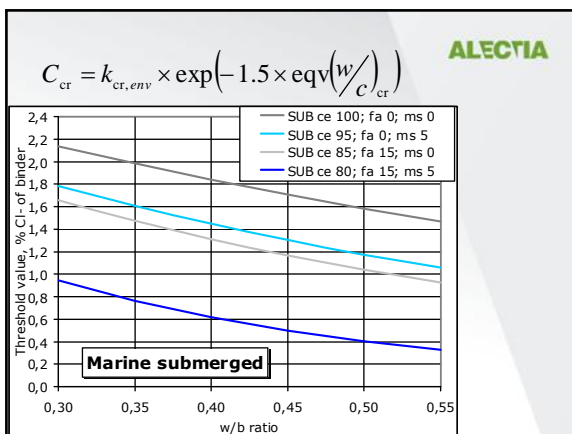
$$eqv(w/c)_{property X} = \frac{w}{C + k_{FA,property X} FA + k_{MS,property X} MS}$$

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### Estimation of the threshold value

**Road environment**

**Marine environment**



The two ways of making the estimation - by a table or by a formula correlate satisfactory - remember they are both estimates!

...and what more do we need?

Are we satisfied now?

*We have been focussed on penetration methods ☺  
- now it is time for initiation methods*

*D and C<sub>cr</sub> deserve the same attention!*

... but can we do it better?

### Why we should make it better?

...because we must:

- Avoid disputes and/or frustration
- Meet the demands for greener production
- ...therefore be able to handle new types of cement and other materials
- Meet the demands for more economical service and maintenance
- ... therefore face the fact that use of service life models will be required more frequently
- Our models are more sophisticated - we have included a time dependence...

### Why laboratory tests?

- We know that a large number of parameters influences the threshold value
- Some have been identified in the lab
- We know there is much more parameters in the real world

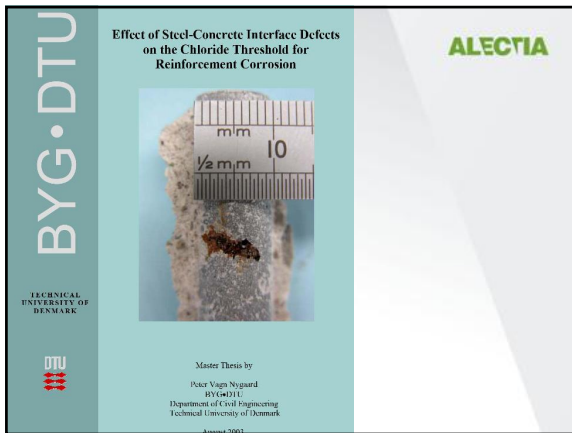
### Why laboratory tests?

- We can try to limit the number of variables in the lab
- When we can reproduce results we can carry on
- With time we will learn more and more about the decisive parameters
- It is a long way to go...
- But we started a long time ago

### Threshold values - the recent development - In Denmark and Sweden - up to 2003:

- 1985-1991 - Birgit Sørensen (and Carolyn M. Hansson) in lab tests.
- 1991-1995 Karin Pettersson and Paul Sandberg - in lab and in Träslövsläge.
- 1993-1999 Hans Arup, Paul Sandberg and Henrik E. Sørensen - multi-probe in lab and in Träslövsläge.
- 1999-2001 NORDTEST project AEC-CBI an attempt to make a standard test method was made.
- 2002-2003 Peter V. Nygaard, master thesis.

...It is all published and in English

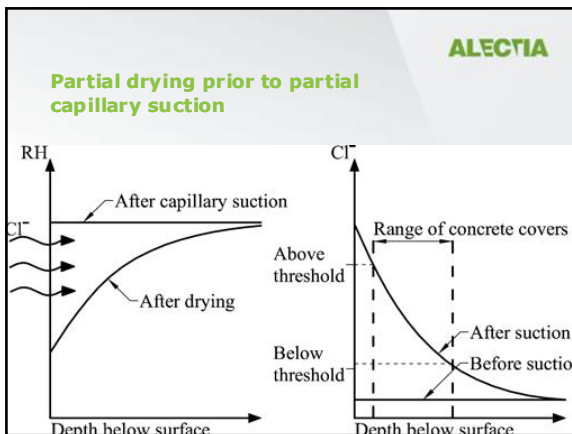


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**The work by Peter V. Nygaard gave a breakthrough, by:**

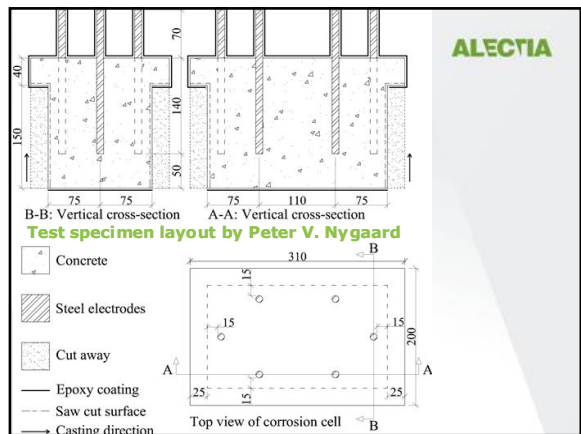
- Accelerating chloride ingress by first drying the test specimens in a controlled climate...
- ...after which the specimens were exposed to a saline solution allowing capillary suction of the saline solution...
- ...and thereby avoiding the densification due to formation of a dense invisible (to the naked eye) layer of calcite
- Designing the corrosion cell to solve the earlier encountered problems with unwanted corrosion attacks at vital parts of the corrosion cell not intended as anode.

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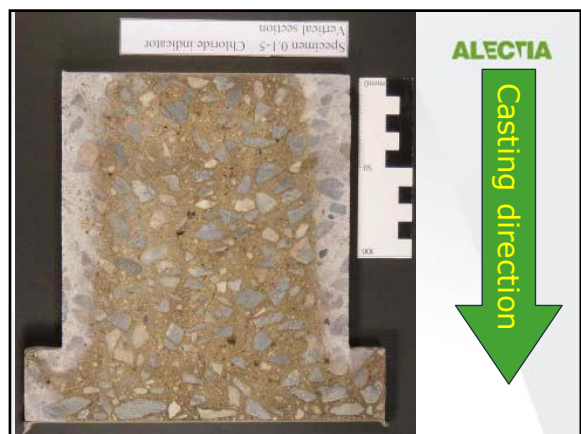
**Partial drying prior to partial capillary suction**



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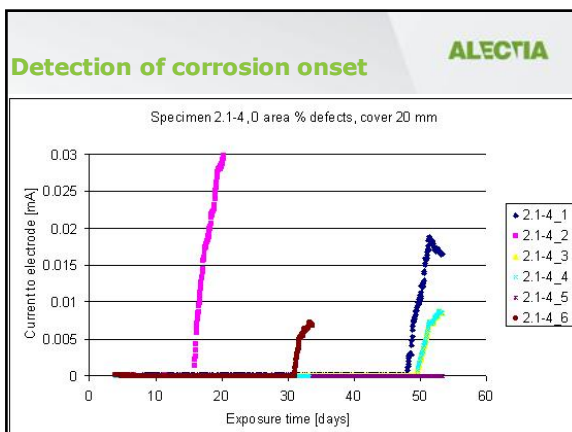
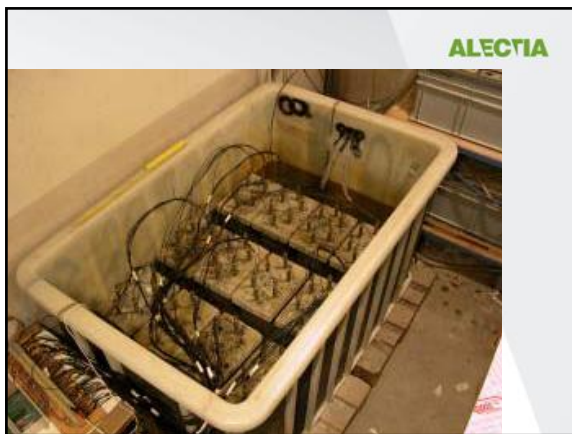
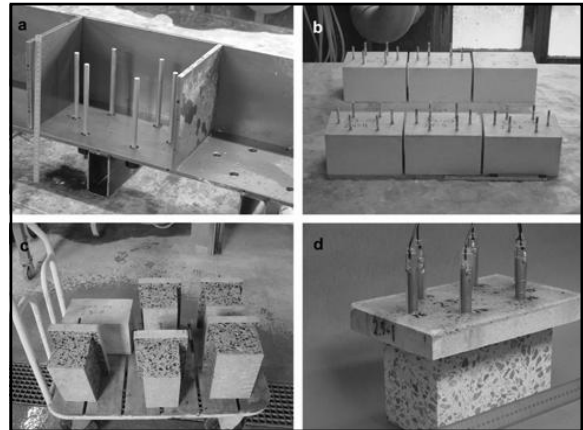


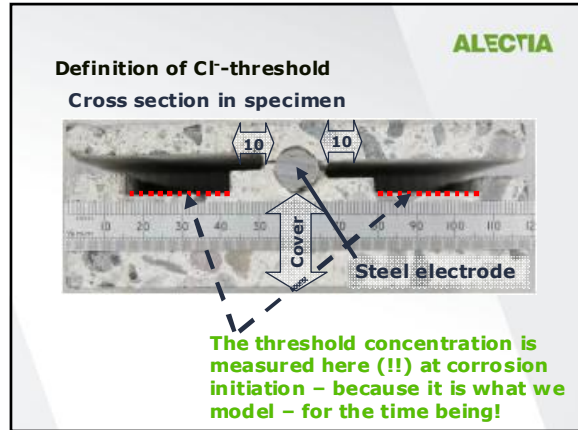
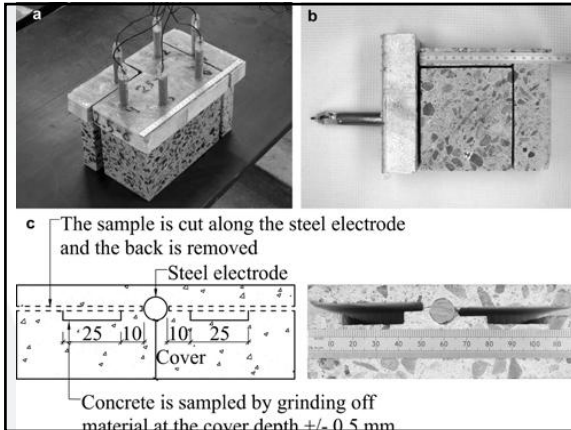
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### Potentiostatic test set-up

- The set-up is used to determine the onset of corrosion
- The current to the counter electrode in order to maintain the potential is monitored
- A sudden rise in current gives the corrosion onset





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**Test principle**

General requirements	Provisional measures
<ul style="list-style-type: none"> <li>■ Shall give repeatable threshold values</li> <li>■ Shall relate to service life modelling</li> <li>■ Shall be rational - i.e. economical and sensible</li> <li>■ Shall also consider existing structures</li> </ul>	<ul style="list-style-type: none"> <li>→ Proven specimen design and procedures</li> <li>→ Measurements in bulk concrete</li> <li>→ Proven equipment and smart conduction of test</li> <li>→ Has to be further investigated</li> </ul>

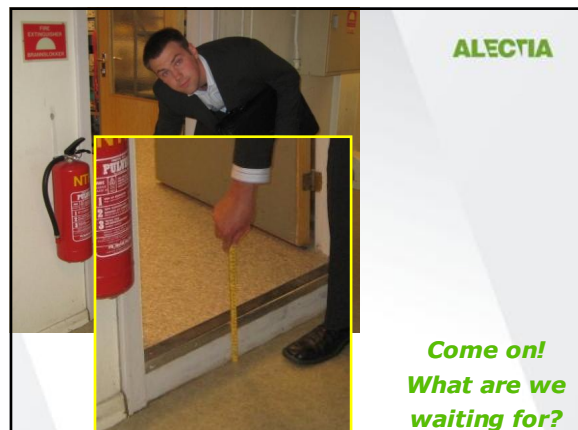
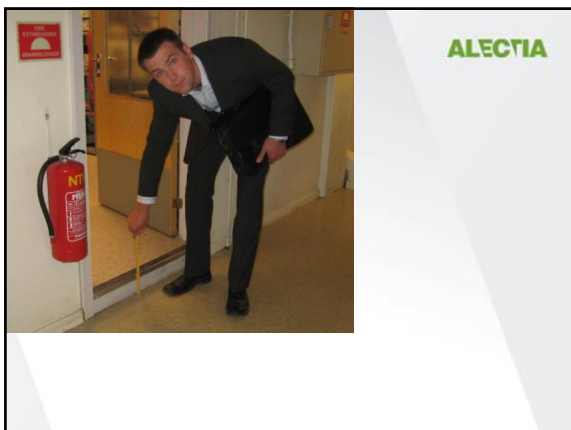
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*We need to know the threshold better!*

*The first step must be to do it in the laboratory*

*Otherwise we will walk like blind people!*

*Peter V. Nygaard showed us how to measure it!*



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