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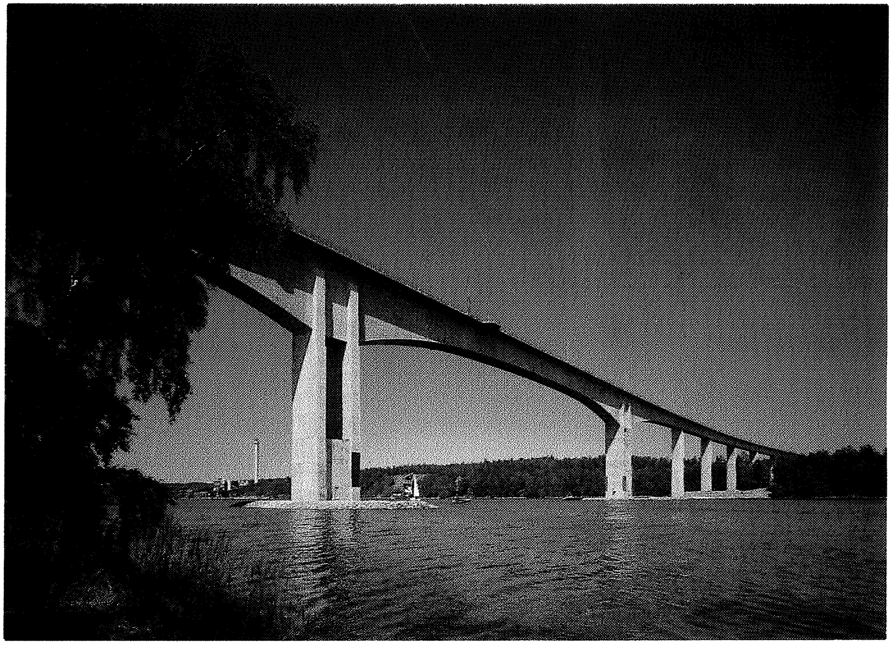

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Critical evaluation of factors affecting chloride initiated reinforcement corrosion in concrete

Paul Sandberg

Report TVBM-3068 **Licentiate Thesis**

SUMMARY

The purpose of this licentiate study was to undertake a critical evaluation of the relative importance of factors affecting (i) the chloride transport into concrete, (ii) the critical chloride concentrations for the onset of active reinforcement corrosion.

Since the topic is naturally very complex, the aim of this work was to present an overall picture of the problem and a guideline for future work rather than presenting detailed information on limited parts of a very large topic.

Research on high quality concrete structures exposed in the field have revealed large variations in the chloride penetration and the corrosion properties of the concrete and its reinforcement. The micro environmental conditions in various exposure zones have been found to be of major importance compared to variations in the concrete itself, providing that the general concrete quality is high.

It was confirmed that the critical chloride concentration for the initiation of active reinforcement corrosion is the most important factor controlling the initiation time for a given concrete structure exposed in a chloride environment. Although experimental data derived from concrete studies are incomplete, the chloride threshold value for a given steel quality is likely to depend on mainly the steel potential, the steel-concrete bonding and the concrete alkalinity, properties which in turn are controlled by the micro environment and the concrete design and quality. The micro climate apparently has a very large influence on the steel potential and the concrete alkalinity, and therefore on the chloride threshold value, for a given concrete design and quality.

Concrete exposed to partial drying in combination with high chloride concentrations is generally most suspectible for chloride induced reinforcement corrosion. Typical examples include concrete exposed for marine environment or deicing salts in the upper splash and salt spray exposure zones. Such semi dry micro environments in the concrete are associated with a high concentration of chloride and oxygen, and a high passive steel potential, and therefore also with a low chloride threshold value.

It is suggested that a selective replacement of ordinary steel for stainless steel would be the most effective way to improve the critical chloride concentration in the most aggressive micro climates. Although quantitative data on critical chloride concentrations are lacking for stainless steel in concrete as well as for ordinary steel, several relative comparisons have indicated a superior chloride resistance for stainless steel in concrete. However, it remains for future research to evaluate the most cost effective types of stainless steel to be used as a selective replacement of ordinary steel reinforcement, including considerations of durability as well as mechanical properties.

A model for the prediction of the initiation time for reinforcement corrosion in concrete is outlined. It is based on long term field observations and supplementary laboratory investigations. The effects of the steel potential, the concrete alkalinity at the reinforcement, and the chloride binding, are accounted for in the model as affecting the critical chloride concentration for the initiation of active reinforcement corrosion.

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The prediction of the long term chloride transport rates into the concrete is currently based on empirical relationships derived from field data. However, it is emphasised that empirical relationships should be replaced, or at least complemented, with a sound scientific model for chloride transport into concrete, taking all relevant factors into account.

Practical consequences for the design of modern high quality structures are discussed, as supported by some experimental field data. A specific use of stainless steel reinforcement in some most aggressive exposure zones is suggested to be evaluated more in detail, since only a small fraction of the total reinforcement would need to be replaced. The hazard of galvanic corrosion as a consequence of connecting ordinary steel to stainless steel embedded in concrete is regarded as negligible. Furthermore, less expensive designs may be used in other parts of the structure being exposed to less aggressive micro climates, thus allowing a more cost effective design of the structure for a given desired service life.

Lund in February 1995

1. INTRODUCTION

1.1 Aim of the study

This licentiate study has been completed as a part of a larger experimental program "Durability of Reinforced Concrete Structures in Marine Environment" carried out in Sweden and Denmark. The aim of this work has been to identify and critically evaluate some major parameters influencing the onset of active reinforcement corrosion in concrete in marine environment.

Literature surveys and/or experimental investigations have been undertaken by the author or by other researchers within the program in order to elucidate the relative importance of various parameters. Since the topic is naturally very complex, the aim of this licentiate thesis is to present an overall picture of the problem and a guideline for future work, rather than presenting detailed information on limited parts of a very large topic.

1.2 Organisation of this report

This report has been divided into Part I - General considerations on chloride initiated reinforcement corrosion in concrete, and Part II - A model for prediction of the corrosion initiation time in reinforced concrete. Part II also include a discussion of optimal materials selection and research needs, and a more detailed presentation of experimental results regarding factors affecting the chloride transport in concrete.

In Part I, an introduction to the steel corrosion phenomenon in concrete is presented in Chapter 2, as well as some general principles for a model for service life prediction of reinforced concrete structures in saline environment. More general information on passivation-depassivation of steel in concrete is given in Chapter 3. The critical chloride concentration for depassivation of the reinforcement in concrete will be discussed more in detail in Chapter 4, followed by information on the concrete pore solution chemistry in Chapter 5.

The effects of some protective measures aiming at improving the corrosion properties of the reinforcement in concrete are briefly discussed in Chapter 6. Such protective measures include organic and metal coatings of the steel, corrosion inhibitors, non metallic reinforcement, selective use of stainless steel and cathodic protection of the steel.

In Chapter 7, a general discussion of the degradation of porous materials is undertaken, as well as a discussion of the effects of environmental impact on chloride permeability of concrete.

In Part II, Chapter 8, a general discussion is undertaken on some factors to be considered in a model for the initiation time for chloride induced reinforcement corrosion. Some experimental evidence from field exposed concrete are presented, as useful information for the model.

A model for the prediction of the initiation time for chloride initiated reinforcement corrosion is described in Chapter 9. It is based on the information on electrochemistry of steel in concrete and chloride transport in concrete, as presented in the previous chapters. Thus, the model is an attempt to combine the present electrochemical knowledge of steel in concrete with the present knowledge of chloride transport in concrete.

At present, the chloride penetration part of the model is based on empirical relationships for the time dependency of chloride transport into concrete. But the ultimate goal is to replace the empirical relationship for a scientifically based model, taking the simultaneous action of chloride transport, moisture transport and micro structural changes into account.

Limited attention will be given to the propagation stage. The state of active corrosion is often controlled by the oxygen supply via rapid micro-structural changes, such as crack formation in the concrete cover. Thus the propagation state is regarded as even more difficult to predict compared to the initiation stage determined by the concrete permeability and the depassivation of the steel.

In Chapter 10, attempts have been made to evaluate the available information in terms of discussions of practical improvements in the design and the materials selection for concrete structures in saline environments. In Chapter 10, suggestions for future research are also presented. A more comprehensive presentation of experimental results regarding the transport of chloride, other ions and moisture is given in Chapter 11.

The information given in Part I-II is mainly qualitative, although some detailed experimental results are presented if available, as illustration to the qualitative discussion. Furthermore, a set of more detailed experimental data is given in the end of Part II.

Part I - General considerations on chloride initiated reinforcement corrosion in concrete

2. CORROSION OF STEEL IN CONCRETE

2.1 General theory of steel corrosion in concrete

Normal reinforcement steel is rapidly passivated when cast into concrete, due to the high alkalinity of the pore fluid in contact with the reinforcement. General information on the stability in water of iron and passivating iron oxides in the absence of aggressive ions such as chlorides is given in Fig. 1 /1-3/. Such Potential - pH diagrams sometimes referred to as Pourbaix diagrams only indicate if corrosion or passivation is thermodynamically possible or not. Such diagrams give no information on the kinetics of any possible reaction.

The steel potential in a given environment represents a balance of cathodic reactions, anodic reactions and any external current from metals in other environments being electrically connected to the steel. The lines a and b denotes equilibrium potentials for hydrogen evolution and oxygen reduction, as described by eq. 1-3.

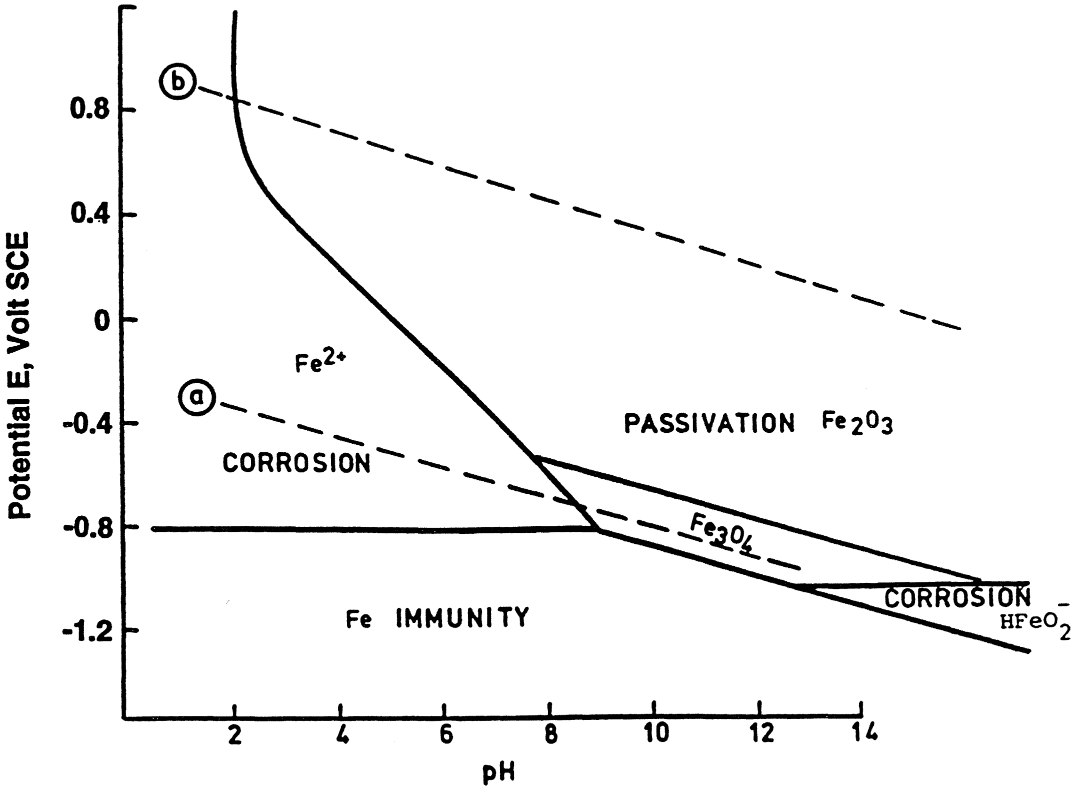


Fig. 1. The stability of iron and its oxides in water at +25°C, as presented in a potential-pH diagram /3/.

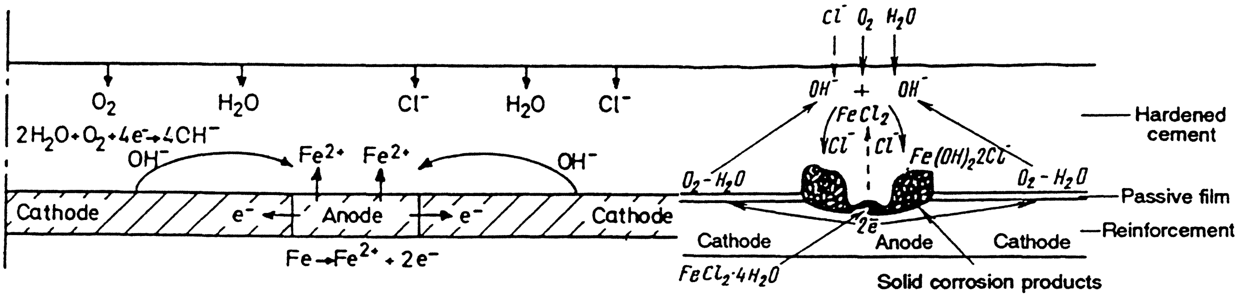


Fig. 2. Illustration of chloride initiated reinforcement corrosion in concrete /20,48/. To the right the catalytic effect of chloride ions is illustrated.

In Fig. 2, a schematic illustration of chloride initiated reinforcement corrosion is shown as presented by Pettersson /20/.

The only cathodic reaction to consider is normally the reduction of oxygen, eq. 1:

$O_2 + 2H_2O + 4e^- \text{--->} 4OH^-$ eq. 1, cathodic oxygen reduction.

In the absence of oxygen or at low pH, hydrogen evolution becomes the dominating cathodic reaction, eq. 2:

$2H^+ + 2e^- \text{--->} H_2$
$2H_2O + 2e^- \text{--->} H_2 + 2OH^+$ eq. 2-3, cathodic hydrogen evolution.

Hydrogen evolution is not possible unless the steel potential is below line a in Fig. 1. Hydrogen evolution may happen in the acid electrolyte in the middle of an anodic pit, which therefore is anode and cathode at the same time. As a consequence, hydrogen induced cracking of high strength steel may occur /16/.

The anodic reactions involve the oxidation of iron, eq. 4, and its conversion to passivating oxides, eq 5-9 or non-passivating hydroxides (rust), eqs. 12-15. Eq. 10 represents the dissolution of iron oxide in the presence of chlorides. The following formulas representing the anodic reactions are very simplified and schematic:

$Fe \text{--->} Fe^{2+} + 2e^-$ eq. 4, anodic oxidation of iron.

$4Fe^{2+} \text{--->} 4Fe^{3+} + 4e^-$
$3O_2 + 12e^- \text{--->} 6O^{2-}$ eq. 5-7, formation of passive iron oxide
$4Fe^{3+} + 6O^{2-} \text{--->} 2Fe_2O_3$

$3Fe + 4H_2O \text{--->} Fe_3O_4 + 8H^+ + 8e^-$ eq. 8-9, formation of passive iron oxide
$2Fe + 3H_2O \text{--->} Fe_2O_3 + 6H^+ + 6e^-$ as presented by Alekseev /48/

$2Fe_2O_3 \text{--->} 4Fe^{2+} + 3O_2 + 8e^-$ eq. 10, anodic dissolution of iron oxide in presence of chlorides

$Fe^{2+} + 2Cl^- + XH_2O \text{ ---> } FeCl_2{*}XH_2O \text{ (s)}$

eq. 11, formation of solid iron chloride proposed to be stable in concrete with low oxygen content /5/.

$Fe^{2+} + 2Cl^- \text{ ---> } FeCl_2 \text{ (aq)}$

eq. 12, formation of soluble iron chloride. Iron chloride is normally considered to be highly soluble at the steel - concrete interface /4,16/.

$FeCl_2 \text{ (aq)} + 2OH^- \text{ ---> } Fe(OH)_2 \text{ (s)} + 2Cl^-$

eq. 13, formation of white rust in oxygen poor concrete

$FeCl_2{*}XH_2O \text{ (s)} +2OH^- \text{--->} Fe(OH)_2 +2Cl^- + XH_2O$

eq. 14, dissolution of iron chloride and formation of rust

$4FeCl_2\text{(aq)} +O_2+ 6H_2O \text{--->} 4FeOOH +8HCl\text{(aq)}$

eq. 15, oxidation of Fe(II) to Fe(III), acidification of pit in presence of chloride ions and oxygen

$2Fe_2O_3 + 4OH^- \text{ ---> } 4HFeO_2^- + O_2$

eq. 16, low potential iron oxide dissolution

$Fe + 2H_2O \text{ ---> } HFeO_2^- + 3H^+ + 2e^-$

eq. 17, low potential iron dissolution

Iron chloride is normally regarded as highly soluble, and then eqs. 11 and 14 are of no practical importance for the liberation of chloride ions.

The catalytic effect of chlorides involves the dissolution of iron oxide, eq. 10, the formation of soluble iron chloride, eq. 12, the diffusion of dissolved iron chloride to hydroxide or oxygen rich areas, and the formation of solid rust, eqs. 13, 15. Chlorides are thus released for a new attack on the iron oxide or the naked steel.

The catalytic effect of chlorides is much stronger in the presence of oxygen, since the chloride attack is then accompanied by a very aggressive local acid attack as described in eq. 15. pH as low as 1-2 has been observed in corrosion pits, indicating a strong acid dissolution of steel. All corrosion products are kept in solution at such low pH. Some concrete is dissolved by the acid attack as well. Since little or no expansive solid corrosion products are formed in the acid environment, the pitting corrosion may propagate rapidly but unnoticed from the outside /4,16/.

The white iron hydroxide formed at low oxygen concentrations is rapidly destroyed when exposed to air.

Some researchers believe that the catalytic effect of chlorides is inhibited at very low oxygen concentrations due to the formation by solid iron chloride, eq. 11, thus terminating the chloride attack on iron oxide or steel. If later exposed to oxygen, iron chloride is rapidly converted to rust, eq. 14, releasing chlorides and initiating a rapid corrosion attack on the remaining iron oxide and steel.

The anodic and cathodic reactions for passive steel in concrete have been graphically presented by Hansson /3/ in Fig. 3. $E°_O$, $E°_H$ and $E°_{Fe}$ denotes the equilibrium potentials at which oxygen, hydrogen and iron would be stable if not in contact with each other.

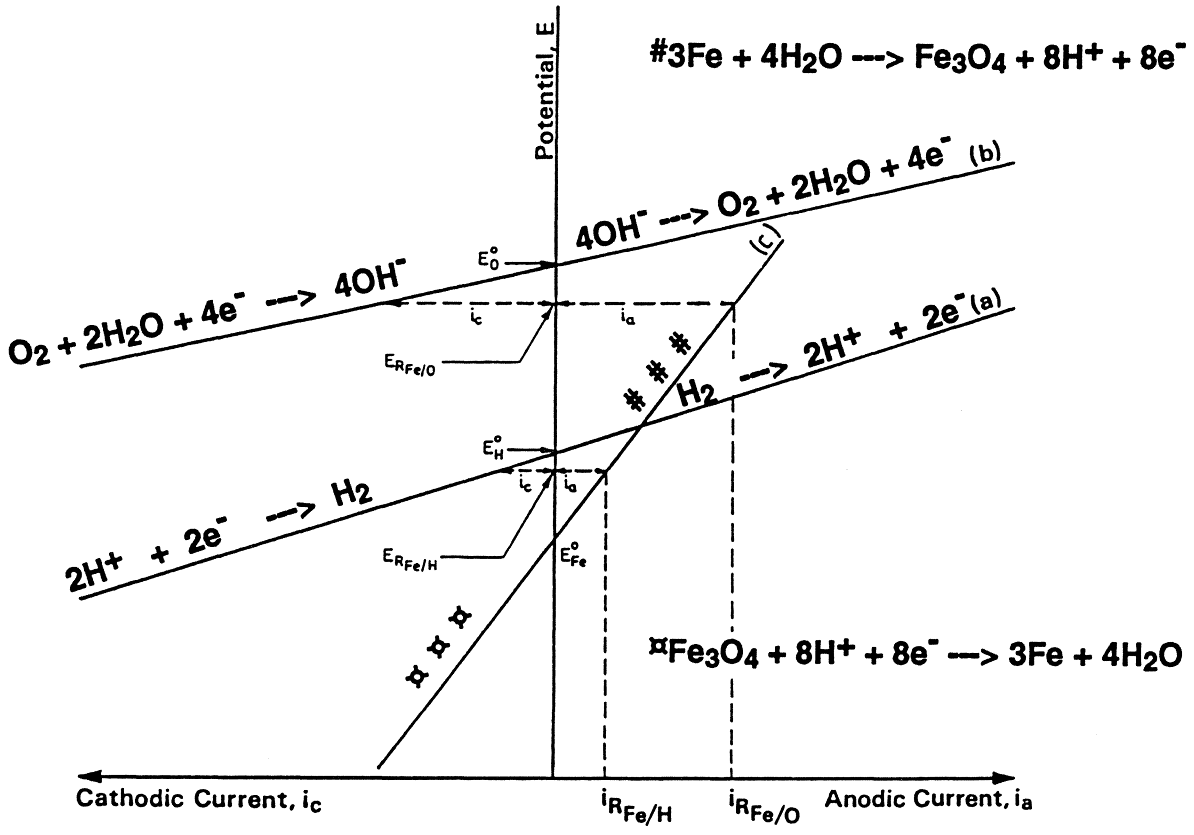


Fig. 3. The potential/current relationship for anodic and cathodic reactions passivating steel in alkaline solutions such as in concrete /3/.

If iron and oxygen react in an alkaline solution, the potential at the steel surface will reach a value $E_{RFe/O}$, where the cathodic current , i_c, from the reduction of oxygen (line b) will be equal to the anodic current, i_a, from the oxidation of iron (line c).

If iron instead reacts in an alkaline solution free of oxygen, the potential at the steel surface will reach a lower value $E_{RFe/H}$, where the cathodic current , i_c, from the formation of hydrogen (line a) will be equal to the anodic current, i_a, from the oxidation of iron (line c). Since iron oxide is not stable at very high pH and very low potentials (the $HFeO_2^-$ area in Fig. 1), active corrosion will occur, but at a very low rate $i_{RFe/H}$, eq. 16-17 as illustrated in the centre of Fig. 4.

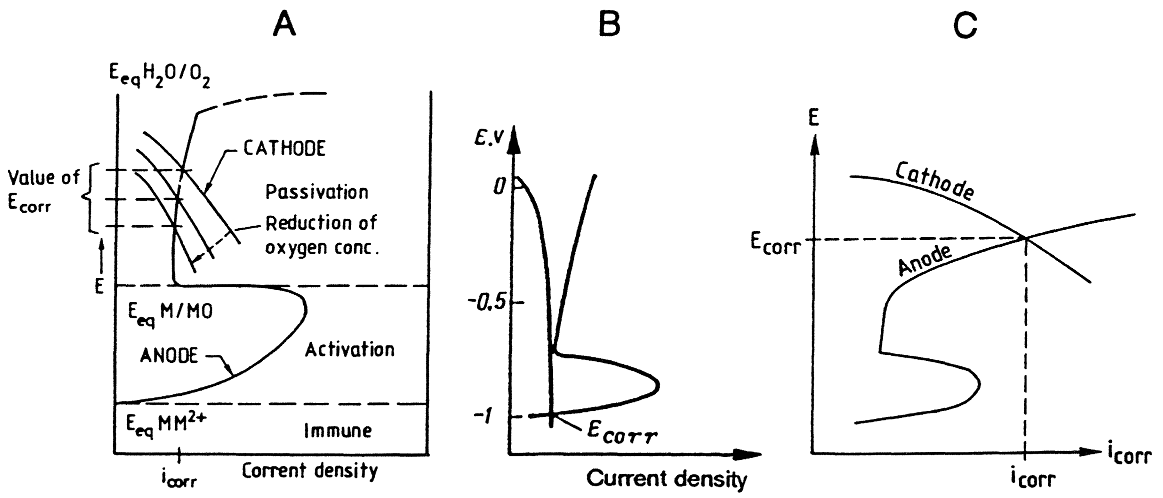


Fig. 4. Schematic illustration of the potential as influenced by the anodic and cathodic reactivity /48/. For a passive steel I_{corr} denotes the passive current required for the build up and maintenance of a passivation oxide layer. (A): The influence of the oxygen supply on the passive corrosion rate and potential. (B): The state of the active low-potential, low-rate corrosion of steel in concrete. (C): Active corrosion on chloride depassivated steel in concrete with high oxygen content.

Anodic reactions tend to decrease the steel potential (electrons are released according to eq. 4) and cathodic reactions tend to increase it. The net result, the steel corrosion potential, is the sum of these so called polarisation effects as illustrated in Fig. 3 and 4. In environments with high oxygen concentrations, the steel potential is high, Fig. 4 (A), approaching the equilibrium potential for oxygen reduction, line b in Fig. 1.

If the oxygen supply for the cathodic reaction is restricted, as when initially available oxygen has been consumed by the formation of a thick iron oxide layer on the steel surface in submerged concrete, the steel potential becomes cathodically controlled.

An illustration of the oxygen availability in concrete long term submerged in sea water is given by Fidjestøl and Nilsson in Fig. 5 /40/. Note that this figure is schematic. No quantitative data are available for the processes indicated. However, numerous measurements of very low corrosion currents have been reported for steel in submerged marine concrete /6/, thus indicating the low oxygen supply for the cathodic reaction.

The passivation of steel in concrete is caused by the formation of a stable layer of iron oxides on the steel surface. The nature of the passivating oxide films formed on ordinary steel in alkaline solutions have been extensively studied in the corrosion science /1-4/. However very limited information exists on the long term behaviour of the passivating oxide film formed on the reinforcement in concrete /5/.

It must be noted that the chemical environment affecting the reinforcement in concrete may be varying and very different from the one described in Fig 1.

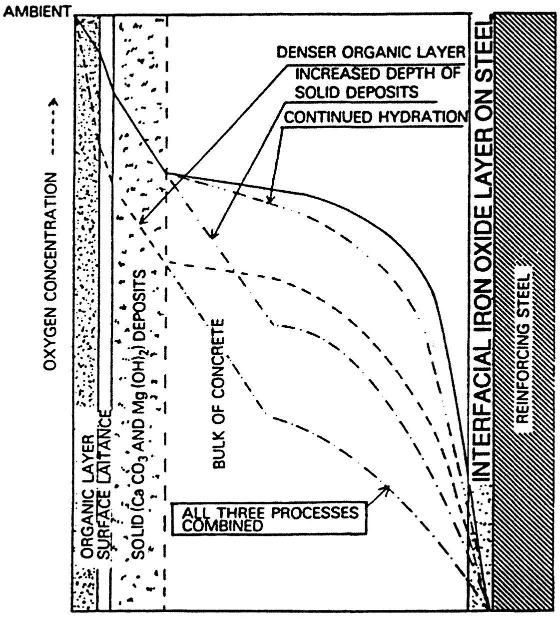


Fig. 5. Oxygen gradients in concrete submerged in sea water /40/.

For ordinary steel in alkaline solutions, the growing oxide layer decreases the passivating corrosion rate with several orders of magnitude, to extremely low levels with no practical significance. The passivating oxide layer is maintained by this extremely slow corrosion process, which consumes oxygen for the transfer of metallic iron to passivating iron oxides; a process that is described by eqs. 4-9.

Fig. 1 indicates a stability region for the passivating oxide layer at pH values ranging from 9 to 13 in the absence of aggressive ions. If the protective oxide layer would crack in the stable pH region, it would immediately repassivate, since the only reaction taking place would be the formation of new repassivating iron oxides.

In an iron-water system such as that described in Fig. 1, a pH < 9 would be required to initiate active corrosion. For normal concrete in the absence of chlorides, such depassivation would be achieved by the carbonation of solid calcium hydroxide and calcium silicate hydrates, and the alkaline pore solution containing mainly dissolved potassium- and sodium hydroxide.

The rate of carbonation is very slow for high quality (low water to binder ratio) concrete, especially if it has a high content of calcium hydroxide. Depassivation by carbonation is normally not a major problem for marine concrete structures, therefore this study was focused on chloride initiation of reinforcement corrosion.

Ordinary steel passivated in alkaline solutions behave very similar to stainless steels. When cast into concrete, ordinary and stainless steels are both protected by a passivating oxide film with similar properties. Corrosion potentials found in the passive state are quite similar /26/. The passivity of some low alloyed stainless steel may be disrupted by aggressive halogenide ions such as chlorides. Sulfides are known to accelerate the corrosion attack on stainless steel exposed for chlorides /1/. Significant concentrations of sulphide have been found in expressed pore solution from slag cement concrete /7,8/, but not in Portland cement concrete due to its oxidising properties at early ages.

For high quality concrete with very slow carbonation rates, chlorides is the main aggressive ion causing depassivation of ordinary steel or low alloyed stainless steel. Little attention has been paid on the depassivating properties of other ions such as sulphides and sulphates. Some experimental evidence do exist however, indicating altered and maybe less effective passivation of ordinary steel in slag cement concrete containing sulphides /7/.

On the other hand ordinary steel is known to passivate very efficiently in normal concrete, in spite of sulphates present in the concrete pore solution. However, the sulfate concentration in the concrete pore solution is very low except at the very first hours after casting, or very close to the concrete surface in sulfate rich environment.

2.2 A model for service life prediction of reinforced concrete structures in saline environments

As presented by Tuutti, reinforcement corrosion in concrete is a two step procedure, see Fig. 6 /8/. If the reinforcement is originally properly passivated in a chloride free concrete, chlorides must be transported in sufficient concentration from the exposed concrete surface, penetrating the protective concrete cover, to reach the passivated reinforcement.

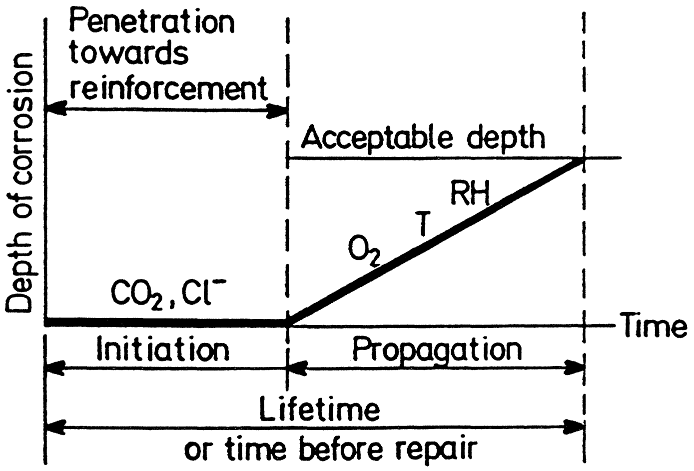


Fig. 6. The initiation and propagation model for reinforcement corrosion in concrete /8/. The model indicates a rapid and often localised pitting type of corrosion occurring in concrete exposed to the atmosphere.

The initiation time depends on (i) how fast aggressive chlorides are transported to the reinforcement, and (ii) which concentration of aggressive chlorides the reinforcement can tolerate before depassivation of the protective oxide layer takes place, as illustrated in Fig. 7 /9/.

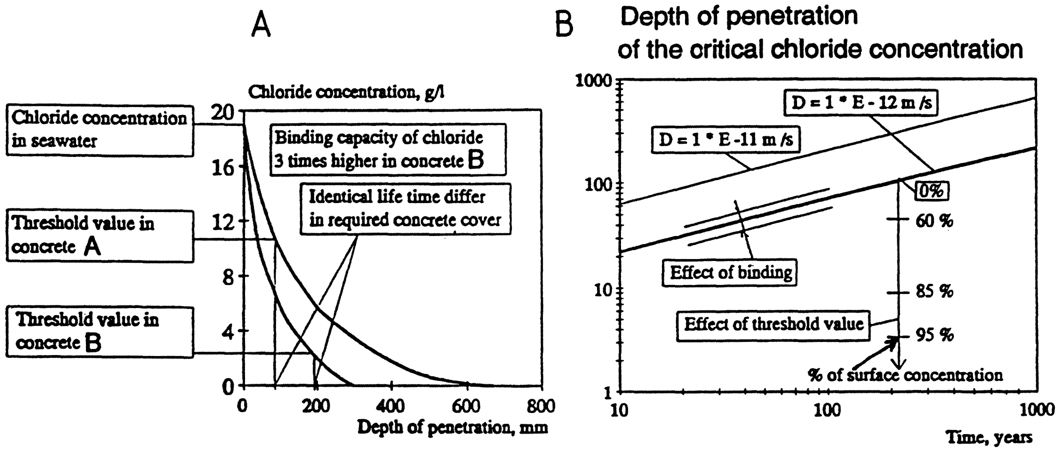


Fig. 7. (A): Effects of varying chloride transport rates and varying critical chloride concentrations for corrosion initiation on the required cover size for a given service life of a structure. (B): Relative effects of various factors affecting the service life for a concrete structure. This figure indicates that the critical chloride concentration has the most decisive influence on the service life /9/.

The passive - active type of corrosion model described by Tuutti in Figs. 6-7 represents the initiation and propagation of reinforcement corrosion in concrete exposed to the atmosphere. In such concrete, enough oxygen is available at the steel surface to maintain high corrosion rates, especially if the attack is concentrated to small areas of very high corrosion activity, i.e. pitting corrosion. Such chloride initiated pitting corrosion is typical for concrete exposed to the atmosphere.

The active corrosion behaviour is remarkable different if the oxygen supply to the reinforcement is restricted, such as when the oxygen supply is restricted in submerged marine concrete. The practically very dangerous pitting corrosion of steel is then impossible as discussed more in detail later in this study. Provided that the oxygen supply for the cathodic reaction remains at a very low level, the net corrosion rate will be practically insignificant as illustrated in Fig. 8.

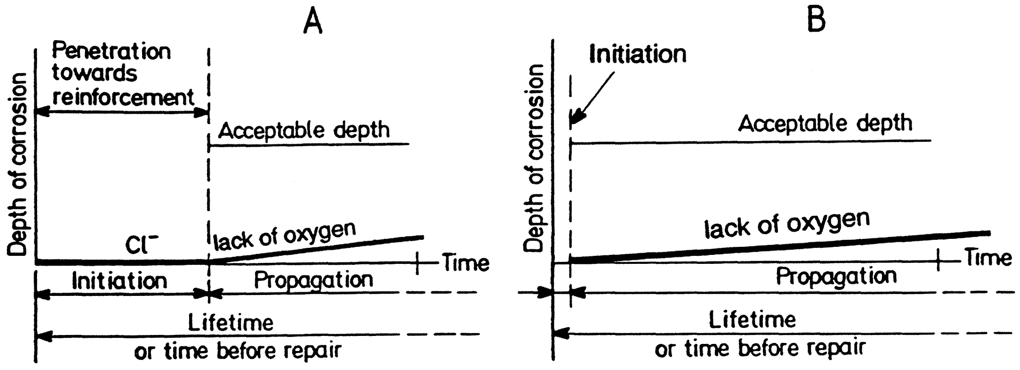


Fig. 8. Corrosion initiation and propagation in concrete with a restricted oxygen supply at the reinforcement. (A): Initially passivated steel is activated, but the corrosion rate remains very low due to a lack of oxygen. (B): The active low potential - high pH type of corrosion is activated after quite short exposure times as indicated in Fig. 1. The possible cathodic reactions including hydrogen evolution are not causing any corrosion rates of practical significance for steel in concrete.

3. PASSIVATION AND DEPASSIVATION OF STEEL IN ALKALINE CONCRETE

3.1 General

A larger portion of the work presented in this study has been focused on properties of concrete exposed in the marine environment. However, the passivation and depassivation characteristics of the reinforcement, are probably of major importance when evaluating factors influencing the service life of all reinforced concrete structures, no matter the type of exposure. Therefore, the main effort has been put into the qualitative discussion of passivation and activation of steel in concrete.

More qualitative and especially quantitative research is certainly needed in this area, as the subject of passivation and depassivation has been overlooked in concrete science. Chapters 2-4 should therefore be regarded as sometimes speculative, with the purpose of encouraging more research activities.

The oxide film on ordinary steel in alkaline solutions is believed to be extremely thin. A thickness of 10-50 Å is reported in the literature /1-2/. The micro structure and the chemical composition of the oxide film depends on the chemical environment, as described by the pH, the potential of the steel and the oxygen pressure.

Apparently, solutions rich in oxygen favours the formation of oxide with a high content of oxygen, Fe_2O_3, at a higher potential. As the oxide film grows, the oxygen pressure, as controlled by the oxygen permeability of the film, and the steel potential drop, resulting in the formation of more Fe_3O_4 (Magnetite) on the expense of Fe_2O_3 /5/.

The oxygen pressure and the potential of the steel in concrete are likely to fluctuate, depending on the environmental impact expressed in terms of the moisture state and the temperature of the concrete. When considering ordinary steel in concrete, a spinel Fe_3O_4 -gamma Fe_2O_3 solid solution has been considered as the major composition of the oxide layer formed /5/, but clusters of Ca $(OH)_2$ have occasionally been observed /10/. The porous spinel structure of the iron oxide layer is believed to favour a film growth in the passive state /5/.

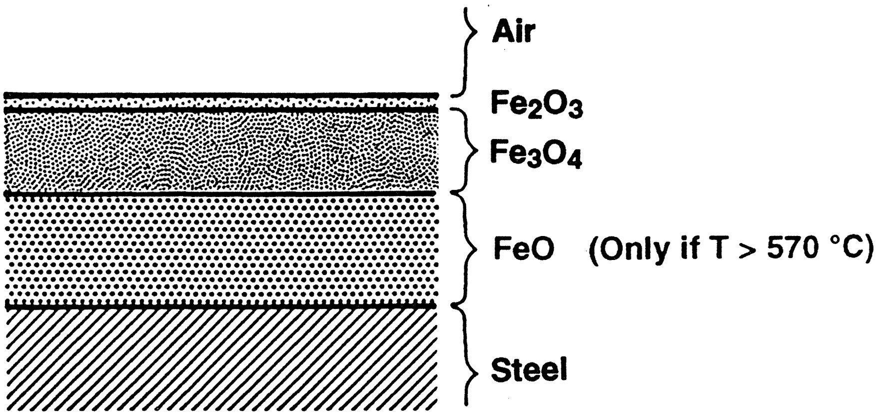


Fig. 9. An approximately 50 microns thick layer of iron oxides, the "scale", is formed by the hot rolling process of ordinary steel /1/.

Hydrating cement will at early ages considerably affect the composition of the pore solution and the moisture state of the concrete. Furthermore, calcium hydroxide is known to deposit at the steel-concrete interface at early ages of the concrete. These factors are likely to affect the micro structure and the composition of the oxide film as compared to the film arising in alkaline solutions in a constant chemical environment. Nevertheless, it may as a first attempt be useful to base a model for the passivation of ordinary steel in concrete on existing models for ordinary steel in alkaline solutions.

Normal reinforcement in concrete is made from hot-rolled black steel. The hot-rolling is known to form an approximately 50 microns thick surface layer of iron oxides termed scale. The composition of the scale is not very different from the oxide film formed in alkaline solutions, as illustrated in Fig. 9. Note that FeO does not form below + 570 °C.

Furthermore, recent studies on the passive oxide layer found on ordinary steel in old concrete have revealed a sometimes hundreds of microns thick layer of iron oxides /5,10/. Such a very thick oxide layer is normally considered as being a less efficient passivation compared to ideal thin layers, since a thick and rapid growing layer is associated with quite high ion permeability. The oxygen and/or ferric ion permeability through the oxide layer is controlling the rate of growth. /1/.

However, recent studies /10/ have indicated that the relatively high growing rate of the oxide layer, i.e. high oxygen and/or ferric ion permeability, does not necessarily mean high permeability for chloride ions, as discussed further in Chapter 3.

In /5/, most ordinary steel in concrete is regarded as belonging to a "semi-passive" state, as partly protected by this quite thick but very inhomogeneous and in most environments probably quite permeable oxide layer. Corrosion products from active corrosion (rust) have been found in the outer parts of this oxide layer /5,10/. Apparently this "semi passivating" oxide layer may grow thicker with time, as opposed to the normal passive oxide film found on black steel in alkaline solutions.

Steel			
	Fe		
	$Fe_{1-x}O$	70%	
Scale	Fe_3O_4	20%	~50 µm
	αFe_2O_3	10%	
Passive oxide film	$Fe_3O_4 + Fe_2O_3$ film no well defined micro structure		~10-50 Å (1-5E-3 µm)
Iron oxide layer	Fe_3O_4	"Spinel"	
	γFe_2O_3		~50-200 µm in old concrete
	$Fe(II)(OH)_2$		growing with time
	$Fe(III)OOH$		
Concrete	$Ca(OH)_2$		

Fig. 10. Initially separated iron oxide phases on ordinary steel in concrete at early ages.

As indicated, it is not known if the original oxide layer from the hot rolling of ordinary steel, and the rust phases initially found on most reinforcement, and also the initial passivating oxide film presumable formed in young concrete, remain as separate phases over time as illustrated in Fig. 10.

3.2 The influence of the microstructure at the concrete - steel interface

Steel in concrete is normally much more chloride resistant as compared to when the same steel is exposed to a solution of the same composition as the concrete pore solution. This is true also when the comparison is made at similar steel potentials. The difference in chloride threshold levels can be orders of magnitudes /6/.

The reasons for the improved chloride resistance for steel in concrete as compared to steel in alkaline solutions, at similar steel potentials, are not fully understood. Experimental work by Yonezawa et al /120/, including variations in the bonding between the steel and the cement matrix, have indicated that the effect of physical adhesion between cement hydrates and iron oxides formed on the steel surface is most important. It was concluded that the formation of voids at the steel-mortar interface is a necessary condition for active corrosion to start in concrete with moderate chloride content. Furthermore, observations of the protective effect of calcium hydroxide precipitated at the steel surface were reported in /120/. The protective effect of calcium hydroxide was attributed to the dissolution of calcium hydroxide crystals close to emerging pits, thereby preventing the pH drop in the pit.

Recently a project have been initiated at the Swedish Institute for Metal Research, aiming at studies of the nature and the protective properties of the transition products formed at the steel - concrete interface in concrete exposed in various micro climates.

Clearly, more research is needed to elucidate the formation of passivating or semi-passivating oxide layers, and their ability to passivate ordinary steel in concrete. This topic is probably very complex, since local changes in the micro climate and the exposure time seem to affect the formation and the composition of these layers /10/.

A time-, micro structural- and micro environmental dependency of the passivating properties of the oxide film formed on ordinary steel in concrete would indeed help to at least partly explain the large scatter found in the concrete literature as regards the chloride threshold levels for the initiation of active corrosion.

3.3 The catalytic effect of chloride ions on the depassivation of ordinary steel in concrete

At high chloride concentrations at the surface of the reinforcement in uncarbonated concrete, chloride ions will ultimately penetrate the passivating oxide layers, thus initiating active corrosion. The corrosion rate increases with orders of magnitudes when a formerly passivated steel turns active. This shift in corrosion rate provides a convenient way of studying passivation-depassivation by monitoring the corrosion current or the magnetic field induced by the corrosion current.

Very limited information exist on the ability of the described thick oxide layers formed on ordinary steel in concrete, to protect the steel from active corrosion. In /10/, very high levels of chloride, > 2% by weight of cement, were found at the outer parts of the oxide layer. However, the oxide layer apparently still served as a barrier for chloride and maybe also for oxygen transport to the steel surface. Fig. 11 shows relative concentration micro profiles of Fe and Cl obtained by SEM-EDAX through the oxide layer. The Fe concentration is ~100% in the steel and the Cl concentration was found to be approximately 0.4% by weight of concrete at the reinforcement /10/.

No visible corrosion products in terms of black or brown iron(III)hydroxide was found at the visual inspection of the steel surface. However, white iron(II)hydroxide was frequently seen indicating that active corrosion did occur, but a an oxygen concentration low enough to prevent pitting corrosion. The low oxygen concentration at the reinforcement, as indicated by the presence of iron(II)hydroxide, was confirmed by a very low corrosion rate measured in all parts of the structure by normal electrochemical measurements such as polarisation resistance or anodic pulse /11/.

Several researchers have on the other hand indicated chloride concentrations less than 0.05% by weight of concrete as necessary for the initiation of rapid corrosion /5/. However, these results appear to be derived from environments rich in oxygen, and they cannot therefore be compared to the conditions in a submerged concrete of reasonable quality.

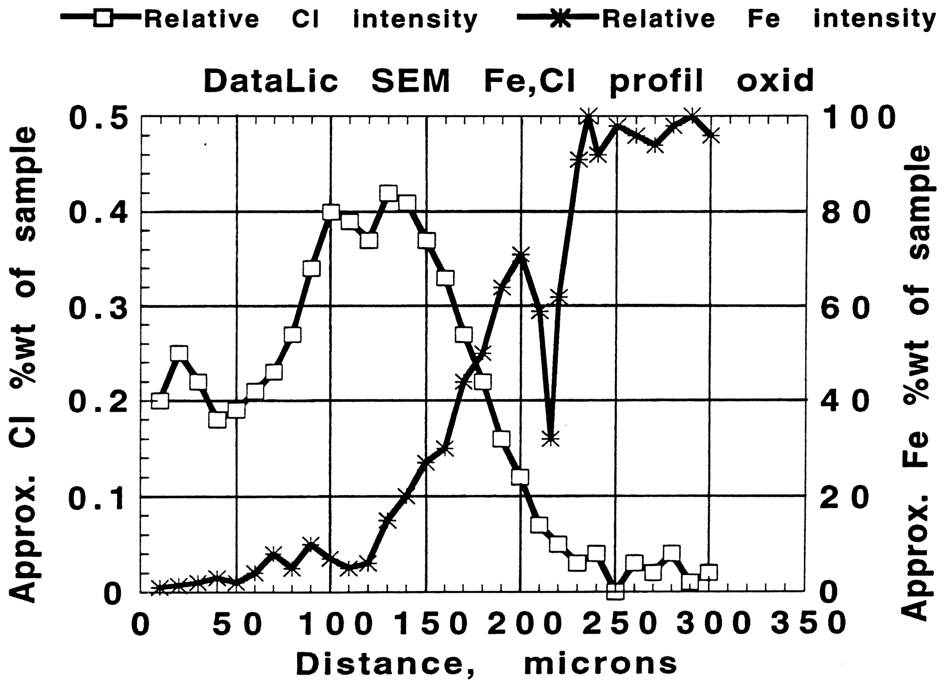


Fig. 11. Micro profiles of Fe and Cl through the approximately 100-150 microns thick iron oxide layer found on ordinary steel in 37 years old concrete submerged in sea water /10/.

As discussed in section 2.1, a certain oxygen availability is necessary in order to oxidise dissolved iron(II) ions further to form Fe(III)OOH (eq. 15), resulting in a strong acidification of the anode. The acidification accelerates the chloride attack substantially /16/. This apparent catalytic role of the chloride ion is however not yet fully understood. It has been suggested /12/ that chloride and hydroxide ions compete for the ferric ions formed in both the passive and active state as described by eq. 4. This theory is supported by the reported pH dependency of chloride initiated depassivation of ordinary steel as reported by Hausmann /13/.

Therefore, it may be argued that the corrosion inhibiting properties of the oxide layer on steel in concrete varies with the oxygen- and the hydroxide concentration in the concrete. Such an argument is not very controversial, since the oxygen concentration is known to affect the steel potential. Furthermore, several researchers /4,48/ have indicated that a relationship between the passive steel potential and the critical chloride concentration for active pitting corrosion exists for ordinary steel in concrete by analogy with stainless steel in saline environment. More details on the parameters affecting the critical chloride concentration for chloride initiated pitting corrosion are discussed section 3.5-3.6 and in chapter 4.

It may also be argued that the micro structural composition of the oxide layer formed on steel in concrete may vary with the micro climate at the steel - concrete interface. Although little information is available on the micro structure of the oxide layers formed on steel in long term field exposed concrete, the available information indicates a long term micro structure which is sometimes very different from the one frequently observed by SEM in relatively young, laboratory made specimens /10/.

Sagoe-Crentsil and Glasser /5/ among others presented another theory on the role of oxygen controlling the catalytic effect of the chloride attack on steel. They reported evidence on the formation of soluble complexes of iron(II)chloride "green rust", if chlorides are present in the iron oxide layer /5/. They also indicated that a certain oxygen availability is necessary for the transformation of green rust to normal iron hydroxide rust. Chlorides bound in the green rust complex are released by the conversion to iron(III)hydroxide, rust, leaving the chlorides free for a new attack on the passivating iron oxide, see eqs. 11 and 14 in section 2.1.

However, in recent studies of old marine concrete /10/, large amounts of white iron(II)hydroxide, but no solid iron(II)chloride, were found. Similar findings have been reported by the Danish Corrosion Institute and elsewhere /14,16/.

It may be concluded that the destructive catalytic effect of chlorides in concrete is much stronger in the presence of oxygen, such as in dry or semi dry concrete, as compared to submerged concrete being very low in oxygen. The effect of pH and oxygen on the chloride aggressiveness on steel in concrete is further illustrated in potential-pH diagrams in chapter 4.

Chloride initiated active reinforcement corrosion in concrete may be divided into three corrosion types as they are discussed in the next sections /4,16/:

3.4 "Electrochemical noise" in sound concrete

The penetration of ions through the passivating oxide layer is concentrated to certain pits, due to the non-uniform permeability of the concrete and the oxide layer. Once a very localised corrosion pit has started, it may again repassivate and reactivate /4/, apparently following the fluctuations in steel potential and oxygen availability, as controlled by the micro climate.

Such transient corrosion events on passive steel in concrete may be recorded as "electrochemical noise" emitted by the steel. Sound concrete has a certain ability to stop the corrosion caused by heterogeneities, and to restore the passivity.

3.5 Chloride initiated pitting corrosion

Chloride ions penetrating the oxide layer at certain pits eventually establish a "corrosion nest", lowering the pH and increasing the corrosion attack at the local pit, see Fig. 12. Pitting corrosion is characterised by the formation of galvanic pairs, with a large passive steel surface acting as cathode next to the very small anodic pits. A rapid increase in corrosion current from the anodic pit makes the surrounding steel cathodically protected, thus concentrating the increasing corrosion attack into the local pit.

The low pH at the pit will keep the corrosion products in solution, allowing diffusion to regions which are rich in hydroxides and oxygen. Eventually, normal rust as ferrous(III)hydroxide and other solid corrosion products, will form.

Pitting corrosion is therefore very dangerous in practice, since the corrosion attack is concentrated to very small areas and since it may take place unnoticed from the outside. Since the corrosion products are soluble in the local acid pit, they can be accommodated without any spalling of the concrete cover.

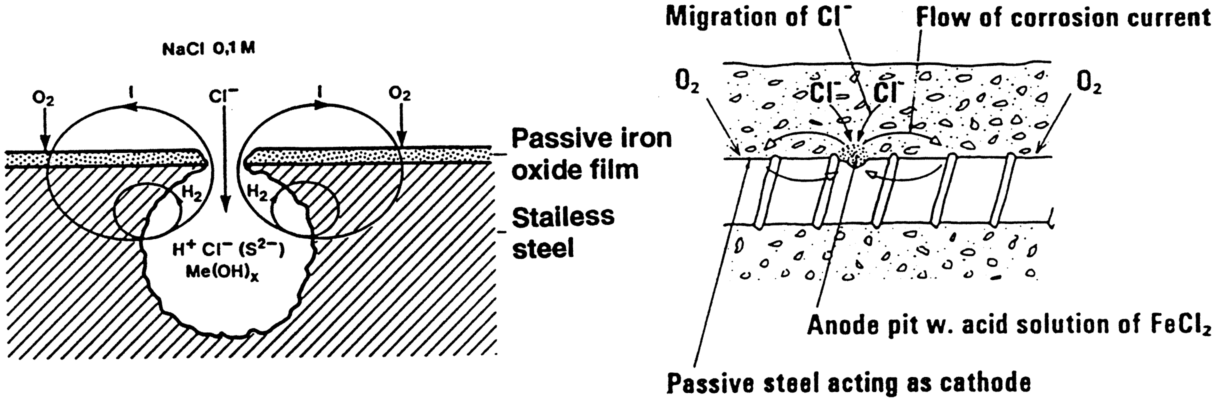


Fig. 12. The development of a localised corrosion nest on the steel as illustrated by Mattsson for stainless steel in saline water /1/ and by Arup for steel in concrete /4/.

Furthermore, the development of a corrosion nest with a local acid environment may favour an accelerated attack. Thus the function of the reinforcement may be rapidly lost even if the total corrosion rate may be quite low. In extreme cases, penetration rates of 5-10 mm/year has been found in the field /16/.

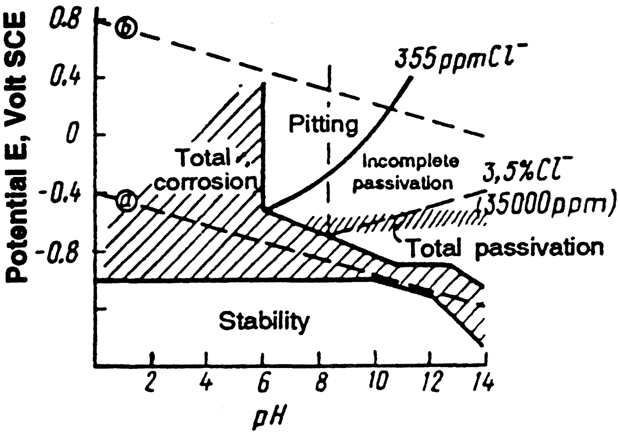
This type of corrosion attack, chloride induced pitting corrosion, is very common for ordinary steel in moist and alkaline environments, such as in concrete exposed in saline environment. The pitting corrosion of ordinary steel in concrete is very similar to chloride induced pitting corrosion of low alloyed stainless steel /4/. Further on in this study, the use of more chloride resistant stainless steel in connection with ordinary steel in concrete will be discussed.

3.6 Critical pitting potentials

Similar to stainless steel, a critical pitting potential exists for passivated ordinary steel in alkaline concrete. The critical pitting potential depends on the alkalinity of the pore solution in contact with the steel /21/, as indicated in Fig. 13. Below the critical pitting potential pitting corrosion cannot be established, since the steel potential would be too low for becoming anodic /4/. Therefore, low potential conditions in high quality concrete is usually harmless in practice.

in

Fig. 13. Potential - pH diagram illustrating the corrosion behaviour of iron ~~is~~ solutions with chloride, as illustrated by Moskvin /21/. Critical chloride concentrations for the development of pitting corrosion are indicated. Pitting corrosion is impossible in and below the area marked "total passivation".



4. CRITICAL CHLORIDE CONCENTRATIONS FOR THE INITIATION OF REINFORCEMENT CORROSION OF BLACK STEEL

4.1 General

The literature on critical chloride concentrations for the initiation of reinforcement steel corrosion in concrete is very conflicting, as illustrated in Table 1 by Pettersson /20,74/. Some critical chloride concentrations for the initiation of stainless steel reinforcement corrosion are presented in Section 4.5.

Table 1. Some critical chloride threshold concentrations for the initiation of reinforcement corrosion as reported in the literature /20,74/.

Researcher	Critical chloride content % by weight of cement	Remarks
Hausmann 1967	0.06-1.0	steel in aqueous solutions pH=12.5-13.2 Cl/OH=0.6
Cady 1978	0.2-0.4	varied with pH
Matsushita 1980	0.8	submarine tunnel
Brown 1981	0.4	varied with cement type
Hansson&Sørensen 1989	0.6-1.4	varied with cement type, curing, water to binder ratio, admixtures, etc.
Schiessl&Raupach 1990	0.48-2.02	varied with cement type and admixtures
Pettersson 1993	0.9-1.8	w/b 0.30-0.40, pH13.0-13.8, Cl/OH=3-6, varied with pH, cement type, pozzolan

The following is a list of some factors contributing to the large spread in critical chloride concentrations found in the literature:

A) Some results are derived from steel exposed to saline solutions, while others are derived from steel embedded in concrete, mortar or cement paste. Several researchers /17,20,120,121/ have reported significantly higher chloride threshold levels for embedded steel as compared to that of naked steel exposed to a chloride solution. Yonezawa /120/ attributed the improved chloride resistance of embedded steel to (i) the interfacial interaction cement paste - steel, as visualised by the thick oxide layer, (ii) the formation of calcium hydroxide in the interfacial zone. The acid action of pitting corrosion may be counteracted by dissolving calcium hydroxide, thus buffering the pH in a local pit.

B) Differences in chloride binding /71/ and the formation of iron oxides /120/ occur when samples are made with cast in chlorides as compared to samples being originally chloride free, everything else being equal. As a consequence, the critical total chloride content found for a given concrete quality varies with the experimental procedure.

C) As previously discussed, the passive steel potential and the alkalinity of the pore solution in contact with the steel most probably have a dramatic influence on the critical chloride concentration measured. However, most of the literature data is presented without this most important information. In some cases measurements or estimations of the concrete alkalinity were made, but the effect of passive steel potential is seldom taken into account. The present situation may be seen as remarkable, since the corrosion behaviour for all metals are more or less related to the potential as expressed in potential - pH diagrams /2/.

4.2 A more systematic approach to the evaluation of critical chloride concentrations

In Fig. 14, the stability limits for the passivating iron oxide Fe_2O_3 on ordinary steel in chloride solutions are indicated for chloride concentrations of 0.01, 0.1 and 1.0 moles/litre (corresponding to 0.355, 3.55 and 35.5 g Cl/litre solution). The stability limits for 0.01 and 1.0 moles Cl/l have been derived by Alekseev /48/, and the remaining line for 0.1 moles was derived using data from the authors indicated in Table 1.

Passive ordinary steel in normal uncarbonated concrete exposed in oxygen-rich environment (such as splash- or salt spray zones, etc.) is indicated in the dotted square /18/. Figure 14 thus indicates that 0.1 mole or 3.55 g/litre chloride would be sufficient to initiate active corrosion on the reinforcement in an oxygen rich concrete.

However, as indicated to the right in Fig. 15, somewhat higher chloride threshold concentrations have been found by Pettersson /14,20/, for ordinary steel in non accelerated testing of concrete and mortars.

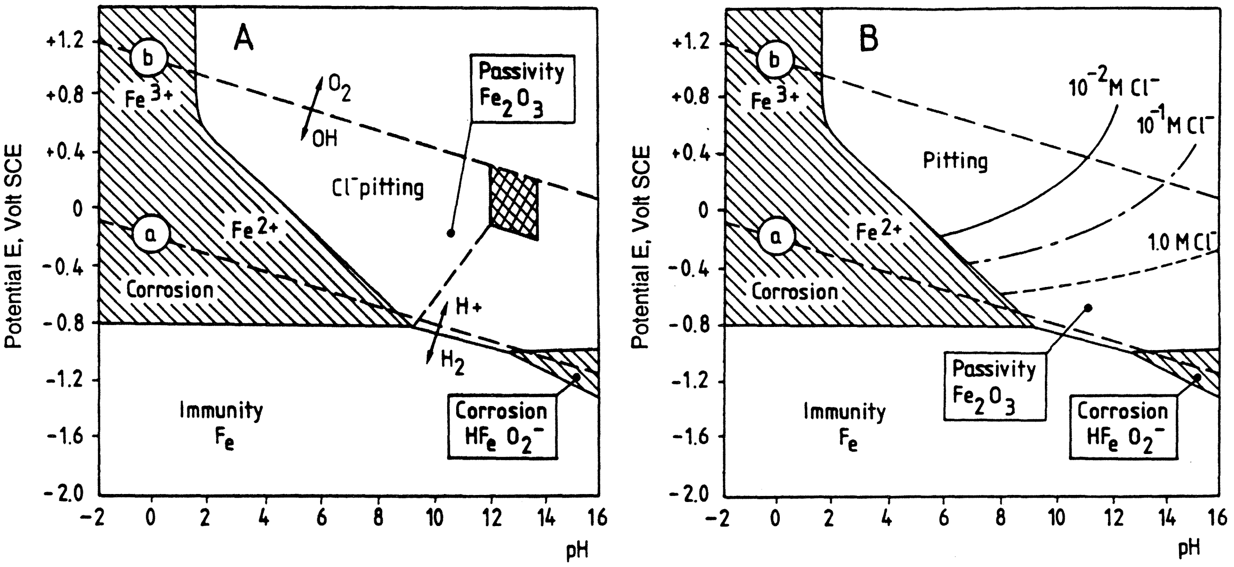


Fig. 14. The stability of iron and iron oxide in chloride solution. (A): A typical concrete in oxygen rich environment is indicated in the square /18/. The critical pitting potential is indicated as a function of the alkalinity of the concrete pore fluid /21/. (B): ISO-concentration lines for critical chloride concentrations 0.01, 0.1 and 1.0 moles/litre are indicated as derived from Alekseev /48/ and Table 1.

Hausmann reported a pH dependency of the critical chloride concentration for initiation of corrosion on ordinary steel in alkaline solutions, see Fig. 15 (A) /13/. These results correspond to the oxygen rich (high potential) area close to line b in Figs. 14 and 16. As previously discussed, several researchers have found a marked oxygen dependency besides the pH dependency for the critical chloride concentration for the initiation of reinforcement corrosion.

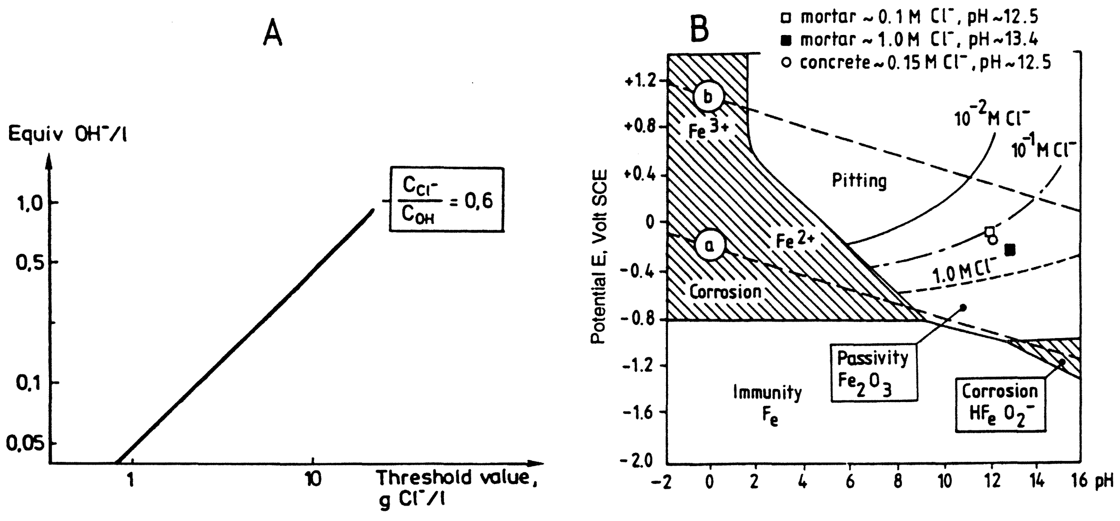


Fig. 15. (A): Critical chloride concentrations for initiation of corrosion on ordinary steel in alkaline solutions according to Hausmann /13/. (B): Critical chloride concentrations for initiation of corrosion on ordinary steel in mortar or concrete as found by Pettersson /14/. The ISO-concentration lines for critical chloride concentrations 0.01, 0.1 and 1.0 moles/litre are taken from Fig. 14.

4.3 The effect of micro climate on critical chloride concentrations

4.3.1 Submerged concrete

Considering concrete submerged into the sea, passive steel potentials as low as -0.4 to -0.9 V relative to the standard Calomel electrode (CSE) have frequently been reported. As illustrated in Fig. 16, such low steel potentials indicate a lack of oxygen and, as previously discussed, a higher chloride threshold value as compared to ordinary steel in concrete with high concentrations of oxygen.

The potential-pH diagrams presented give information on the thermodynamic stability of iron and its oxides exposed for a solution. They do not reveal any information on the rate of corrosion. Only stability or non-stability of the passivating iron oxide is indicated. However, any corrosion process being activated at a passive steel potential as low as - 0.6 to -0.9 V relative to CSE is very slow. Thus, in most cases steel reinforcement in submerged concrete will corrode at insignificantly slow rates even if active corrosion is initiated, provided that the steel is properly embedded in concrete and that the passive potential before initiation is below the critical pitting potential.

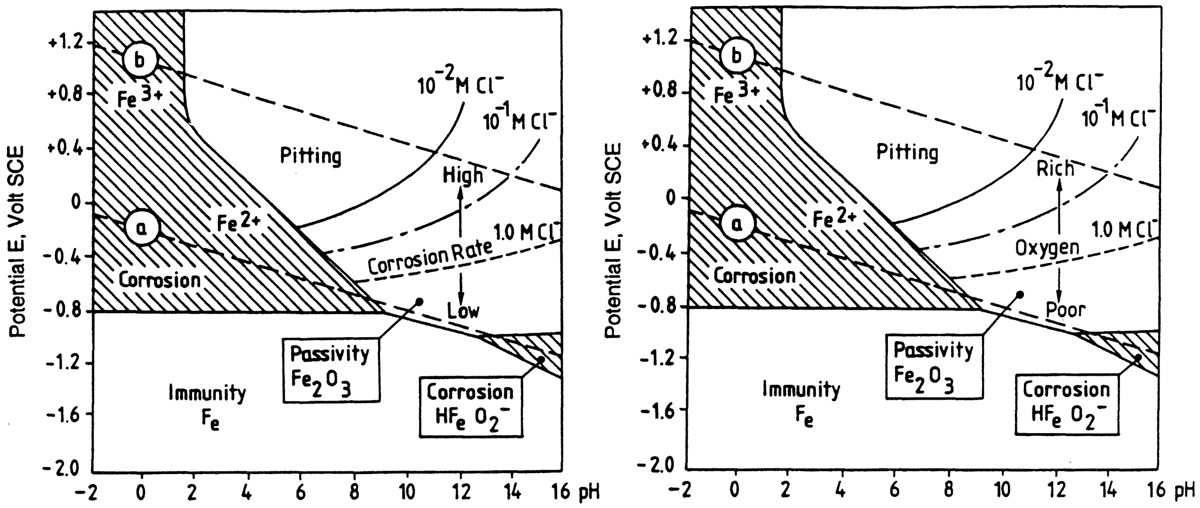


Fig. 16. Expected relationships for ordinary steel in concrete regarding corrosion rate, steel potential, oxygen availability and critical chloride concentrations.

A very low steel potential is maintained by either a lack in oxygen or by an external depression of the steel potential (cathodic protection). Because of low corrosion rates at low steel potentials, it is in most cases not necessary to depress the steel potential into the iron immunity region of Fig. 16. Furthermore, a so called incomplete cathodic protection can be effective at very low currents if applied before the initiation.

At low oxygen availability the corrosion process, if activated, becomes cathodically controlled as illustrated in Fig 4. Since rapid anodic dissolution of iron must be accompanied by a cathodic reduction of oxygen, (the hydrogen evolution reaction is very slow) the lack of oxygen in submerged concrete is a very efficient corrosion inhibitor. As indicated in Fig. 16, active corrosion may occur in the high pH - low potential region, but the effective rate of corrosion becomes practically almost zero.

4.3.2 Concrete in the splash zone and the tidal zone

When considering concrete in the tidal or splash zone, steel potentials have been reported in a very wide range. There are several factors influencing the measured steel potential in concrete which is not water saturated, such as:

A) The concrete resistivity depends largely on the moisture state and on the type and amount of ions in the pore solution. Thus if a reference electrode is placed on the surface of semi dry concrete, a large potential drop in the order of 0.1 to 0.2 V may be measured due to the junction potential between the reference electrode and the reinforcement. If not considered, such junction potential will represent an error in the steel potential measurement /4,15/.

B) Generally, the steel potential is balanced by the cathodic oxygen consumption and the anodic reactions, being either the passive formation of iron oxide or the active dissolution of steel. Since the oxygen availability in concrete is largely dependent on the moisture state /8/, quite small fluctuations in the moisture state may cause rapid shifts in steel potential as illustrated in Fig. 17.

C) Pitting corrosion will cause sharp potential gradients on the steel surface close to the anodic pits. The steel potential measured will represent the average potential determined by a balance between the rate of the cathodic oxygen reduction and the anodic dissolution of steel in the pit.

Bearing this in mind, it is sometimes difficult to evaluate reported steel potential data measured on unsaturated semi-dry concrete using external reference electrodes.

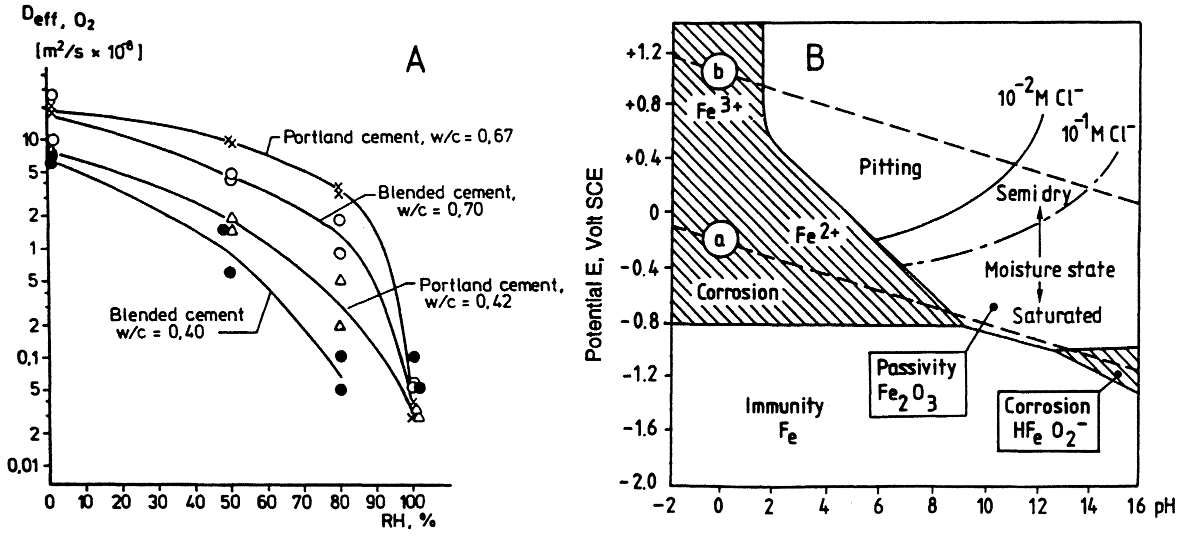


Fig. 17. (A): Oxygen diffusivity as a function of the relative humidity inside the concrete /8/. (B): Expected relationship moisture state - steel potential.

Steel potentials measured in the tidal zone are more easy to evaluate since tidal concrete is submerged twice a day, thus providing very little time for extensive drying. A recent study of tidal zone and submerged concrete exposed for 37 years in Esbjerg harbour, Denmark, indicated passive steel potentials as low as -0.35 to -0.45 V relative to CSE in the tidal zone, and -0.45 to -0.55 V relative to CSE in the upper part of the submerged zone /11/.

Such low steel potentials indicate that pitting corrosion is most likely not a problem to be considered for submerged concrete of high quality with low availability of oxygen.

Considering again Fig. 16, a very low passive steel potential in concrete indicates a fairly high critical chloride threshold concentration and fairly low corrosion rates if the chloride threshold level would be exceeded. Concrete in the tidal zone thus seem to be fairly well protected from rapid reinforcement corrosion, providing that the reinforcement is properly embedded in concrete which is not degraded by other destructive mechanisms. Freezing and thawing combined with erosion is a most effective degrading mechanism for concrete in cold climates /21/.

4.3.3 Concrete exposed to the atmosphere

Most reinforcement corrosion problems do occur in oxygen rich concrete exposed in the atmospheric zone or in the spray zone /24,25/. As indicated in Figs. 16-17, and confirmed by steel potential measurements /6,8/, corrosion is not likely to be inhibited due to a lack of oxygen in concrete exposed to the atmosphere. In very dry concrete such as some indoor concrete, corrosion may be inhibited due to a lack of electrolyte.

The hygroscopic nature of chloride salts, however, will in most cases provide enough moisture for the corrosion process to develop when the concrete is contaminated by chlorides. A typical example is chloride initiated reinforcement corrosion in parking houses, where deicing salts brought indoors by cars rapidly penetrate the dry and often low quality concrete by diffusion and/or capillary suction.

As seen in Figs. 14, 16 and 17, concrete with high oxygen concentrations, with its surface in contact with the normal atmosphere, will be non resistant to reinforcement corrosion as soon as chlorides at low to moderate concentrations reach the ordinary steel.

In order to improve the thermodynamic stability of the steel- iron oxide system in concrete with high oxygen concentrations, one must either reduce the steel potential into the more stable low potential region of Figs. 14 and 16 (cathodic protection), or the iron oxide can be made more stable against chlorides.

"Chloride resistant" stainless steels are made of iron alloyed with chromium, nickel and other species stabilising the passivating oxide layer also in oxygen rich concrete in the presence of chlorides, as discussed in Chapter 6.

4.4 The effect of time and hydration on the chloride threshold values

Looking at Figs. 14-16 and the limited information available on the passivation of ordinary steel in concrete, it may be argued that the critical chloride concentration for initiation of active reinforcement corrosion for a given concrete in a given environment is strongly dependent on the exposure time.

As previously discussed, the chloride blocking and maybe also the oxygen blocking effect of the iron oxide layer formed on steel in concrete may grow stronger with time, thus increasing the apparent critical chloride concentration. However, also some negative effects of time must be considered as discussed below:

Ordinary steel will passivate rapidly due to the very high alkalinity in young concrete, especially if made from Portland cement in the absence of pozzolans. As described later more in detail, however, according to the second law of thermodynamics there will be hydroxide drainage from the concrete occurring in parallel to the chloride ingress. The amount of alkali hydroxides quite rapidly formed in a fresh Portland cement concrete is only about one tenth of the amount of calcium hydroxide formed. Alkali hydroxides are highly soluble and thus very mobile compared to calcium hydroxide.

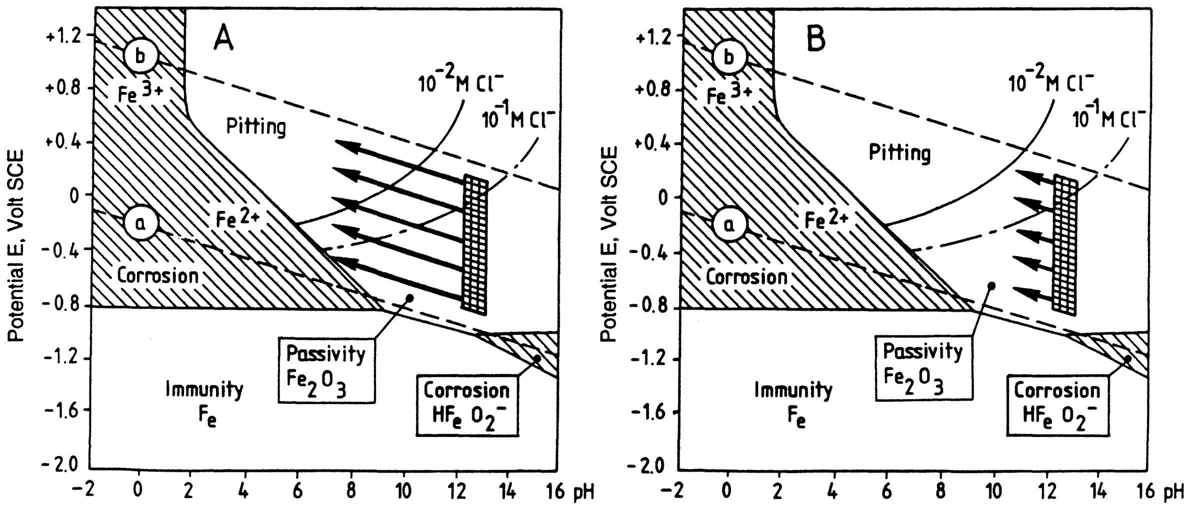


Fig. 18. The effect of a complete removal of calcium hydroxide in the cover on the chloride threshold level, by carbonation (A), or by leaching without carbonation of the calcium silicate hydrate binder (B).

As indicated in Fig. 18, a complete removal of calcium hydroxide from the protective concrete would most probably initiate rapid corrosion if the concrete is carbonated (A). Since the calcium hydroxide content represents the main buffer against rapid carbonation, the calcium silicate hydrate binder in concrete with little or no calcium hydroxide is generally more sensitive to carbonation as compared to concrete with high contents of calcium hydroxide. However, several other factors are of importance, such as the relative humidity and the diffusivity of carbon dioxide.

In carbonated concrete, pH drops below pH 9, often below pH 7, due to the effect of sulphates being released from carbonated calciumsulfo-aluminate hydrates /116/.

A removal of calcium hydroxide without carbonation of the concrete, as would be possible for wet concrete, will not cause such a rapid pH drop, as illustrated to the right in Fig. 18. pH would then remain around 11-12, as maintained by a slow dissolution of calcium from the calcium silicate hydrate, i.e. the binder. However, such a calcium hydroxide free binder would be very sensitive to drying and carbonation, when compared to a binder with an inherent buffer of calcium hydroxide. SEM studies of the steel - cement matrix interface by Yonezawa /120/ made him attribute the protective effect of calcium hydroxide to the dissolution of $Ca(OH)_2$ crystals close to emerging pits, thereby preventing a pH drop in the pit.

4.5 The effect of binding between the reinforcement and the cement matrix on the chloride threshold values

The reasons for the improved chloride resistance for steel in concrete as compared to steel in alkaline solutions, at similar steel potentials, are not fully understood. Experimental work by Yonezawa et al /120/, including variations in the bonding between the steel and the cement matrix, have indicated that the effect of physical adhesion between cement hydrates and iron oxides formed on the steel surface is most important. It was concluded that the formation of voids at the steel-mortar interface is a necessary condition for active corrosion to start in concrete with moderate chloride content.

5 PORE SOLUTION CHEMISTRY AND THE SIGNIFICANCE OF FREE, BOUND AND TOTAL CHLORIDES

5.1 General

The pore solution chemistry in concrete is important, since it is the wet electrolyte and not the total amount of chloride, which affects the corrosion properties of steel embedded in concrete. Furthermore, a better knowledge on the changes in the pore solution composition, and the chemical potentials triggering these changes, in field exposed concrete over the years, may provide some answers to observed deviations from the simple diffusion equations commonly used in concrete science.

No generally accepted and accurate method exists for direct measurements on the pore solution in the high quality type of concrete used today in aggressive environments. As initially developed by Strelkov et al /123/, the pore solution expression method has generally been found to be the most accurate method for studying chlorides and hydroxides in the pore solution of concrete, mortar and paste /76,122,124/. Errors less than 10% have frequently been reported, provided that the amount of expressed solution is not too small, not carbonated and free of colloidal particles. Unfortunately, the pore solution expression method is not applicable for semi dry or very dense concrete.

In the absence of a reliable method for direct studies of the pore solution chemistry in high quality field exposed concrete, a more practical engineering type of method for estimations of free chloride and hydroxide ions are outlined:

5.2 Estimation of critical total chloride content at the reinforcement

Traditionally, total chloride profiles are measured on field exposed concrete, expressed as % total chloride by weight of concrete.

However, since chlorides are bound by the hydrated binder fraction of the concrete only, the amount of hydrated binder, its chloride binding capacity, and the amount of concrete pore fluid, must be known in order to translate a total chloride content in concrete into a free chloride concentration in the concrete pore solution.

In other words, the bound chloride concentration in a hydrated binder (f.i. expressed as % bound Cl by weight of hydrated binder) is assumed to be in equilibrium with a free chloride concentration in the pore solution (f.i. expressed as moles Cl per litre pore solution). In order to translate these concentrations to a concentration of total chlorides in a hydrated binder, the proportion of pore solution in the concrete must be known, e.g. the concrete water filled porosity, or simplified but more practically, the w/b ratio at a given degree of capillary saturation. Furthermore, the degree of binder hydration must be known, since the concrete porosity and the amount of hydrated binder depends on it.

As illustrated in Fig. 19, relationship for the total chloride concentration, by weight of concrete binder, and the free chloride concentration, expressed as moles Cl per litre pore solution, can be experimentally obtained for a given binder type, w/b ratio, degree of hydration and degree of capillary saturation, using the pore solution expression method. This method has successfully been used on cement pastes with w/b ratios as low as 0.30 - 0.35, although the method could not be used on concrete at such low w/b ratios /98,69/. If relationships similar to what is shown in Fig. 19 would be established for laboratory and field exposed concrete and cement pastes at a range of w/b ratios, then it would be possible to extrapolate measured total chloride profiles into free chloride profiles with a reasonable accuracy.

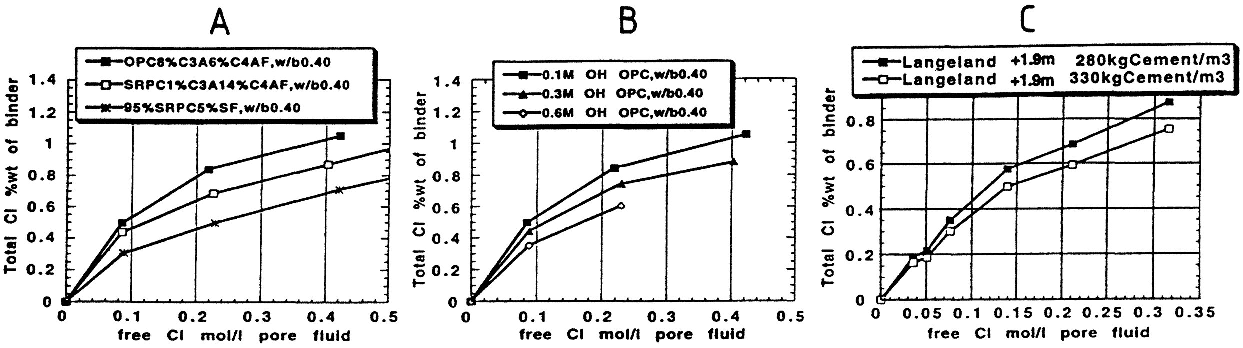


Fig. 19. (A-B): Examples of chloride binding isotherms at 20°C and a degree of hydration of approximately 0.6 /69/. (A): *Influence of various binders at 0.1 M OH⁻.* *(B): Influence of alkalinity of the pore solution. (C): Field estimations of the relationship between total chlorides and free chlorides, for a 15 years old marine upper splash zone concrete, calculated using data from /72/.*

5.3 Some remarks on the chloride binding capacity

The total chloride content usually measured in concrete are usually divided into free, physically bound and chemically bound chlorides, although the distinction between the various types is probably not very clear. Only the concentration of free chlorides affect the corrosion properties of steel in concrete.

However, the concentration of chlorides in a pore solution of a given concrete is controlled by the ability of the binder to fix chlorides, a property which appears to vary with the pore solution composition as indicated in Fig. 19. The alkalinity and the concentration of sulfate ions have been reported to significantly influence the chloride binding capacity of a given binder /69,71,120/. As indicated by Larsson /104/ the chloride binding is most probably influenced by the temperature.

Looking again at Fig. 19, the indicated chloride binding capacity is apparently too low, since total chloride concentrations of more than 2% total chloride by weight of binder have frequently been measured in submerged concrete exposed in the field /64,92/. A total chloride concentration of 2 % by weight of binder would correspond to free chloride concentrations far higher than 0.4-0.55 moles/litre, which is the sea water concentration of chlorides.

The following is a list of factors being known to, or being suggested to, affect the chloride binding capacity of a given concrete quality /69,71,104,125/:

A) The chloride binding capacity of a given binder has been experimentally shown /69,71/ to be affected by the alkalinity and the sulphate ion concentration of the pore solution. Since hydroxide ions are removed from concrete in a similar way as chloride and sulphate ions are transported into it /75/, the chloride binding capacity is affected by the pore solution chemistry, a property which is time dependent.

B) As the binder hydration proceeds for a very long time in concrete with a low w/b ratio, an increased amount of hydrated binder will be available for chloride binding as the exposure time increases. Any self dessication developed will reduce the amount of free water in the pore system, therefore probably affecting the concentration of chlorides and hydroxides among other ions.

C) The physical absorption part of the chloride binding process is assumed to be a fairly rapid process /71/. If the unhydrated clinker phases are hydrated in the presence of chlorides, the aluminate and ferrite phases are known to chemically bind chlorides by the formation of sulfonated aluminate hydrates related to Friedel´s salt /71/, a process which is also fairly rapid.

However, if originally chloride free concrete is exposed to chlorides in the field, most of the ferrite and aluminate phases will form chloride free sulfonated aluminate hydrates related to ettringite and monosulphate when hydrated /111/. When later exposed to chlorides, the chloride free sulfonated aluminate hydrates are likely to convert into, in chloride solutions, the apparently more stable Friedel´s salt. But this process may be slow. As a consequence, the chloride binding capacity of a given concrete would increase over time, as initially chloride free sulfonated aluminate hydrates slowly convert into Friedel´s salt. A schematic illustration of the chloride binding sequences in originally chloride free concrete is proposed in Fig. 20.

D) Carbonation is known to reduce the chloride binding capacity /8/.

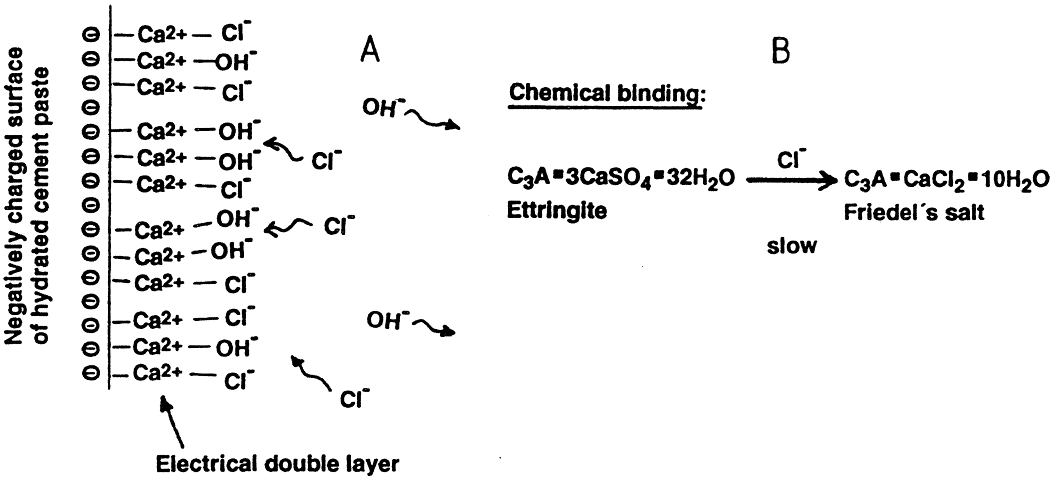


Fig. 20. A proposed model for the time dependency of chloride binding in concrete. (A): Physical absorption of chloride ions on positively charged surfaces. As proposed by Chatterji /87,88/ positively charged calcium ions are absorbed in the electrical double layer next to the negatively charged pore walls dominated by calcium silicate hydrates. Chloride and hydroxide ions compete for the binding sites provided by the calcium ions. (B): Chloride ions are chemically bound by the slow conversion of initially chloride free sulfonated aluminate hydrates into Friedel´s salt.

5.4 Experimental data on changes in the pore solution composition over time

Several researchers, /48,75,120/ among others, have reported a hydroxide permeability of concrete in the same order as chloride permeability. Typical concentration profiles for free chloride and hydroxide ions in field exposed concrete are shown in Fig. 21 /22,43/. Similar profiles found in a laboratory immersion experiment is shown in Fig. 22 /75/.

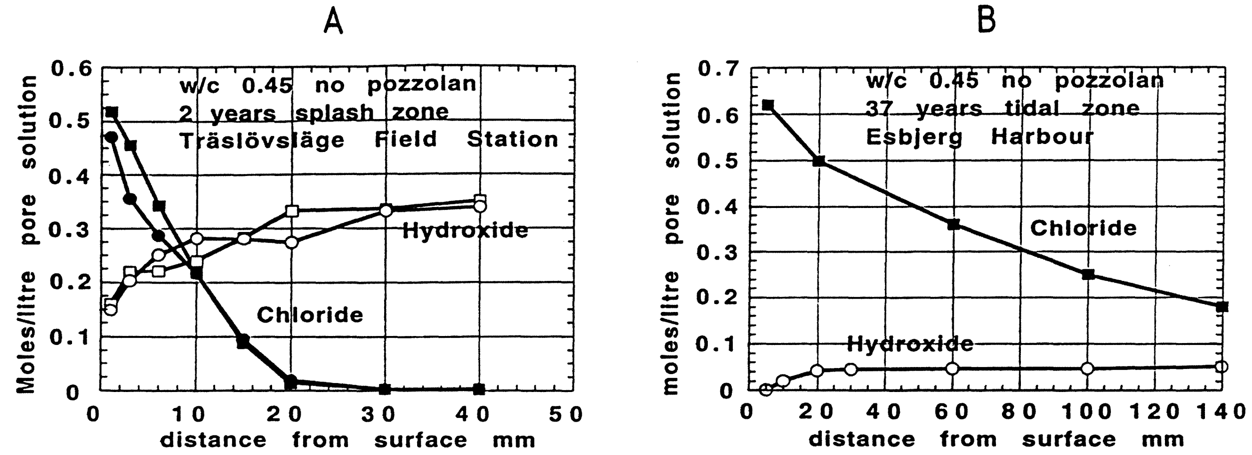


Fig. 21. (A): Hydroxide ions were found to be leached away from a concrete cover as chloride ions penetrate into the concrete, 2 years of marine field exposure. (B): Corresponding ion concentrations found in a 37 years old marine concrete, tidal zone exposure. Note that the data in (A) and (B) are not directly comparable, since the concrete quality, cement type and exposure conditions are not equal /22/.

The hydroxide ion diffusivity has been reported to be either slightly higher or slightly lower as compared to the chloride ion diffusivity, for a given paste or mortar, depending on experimental conditions /75,120/.

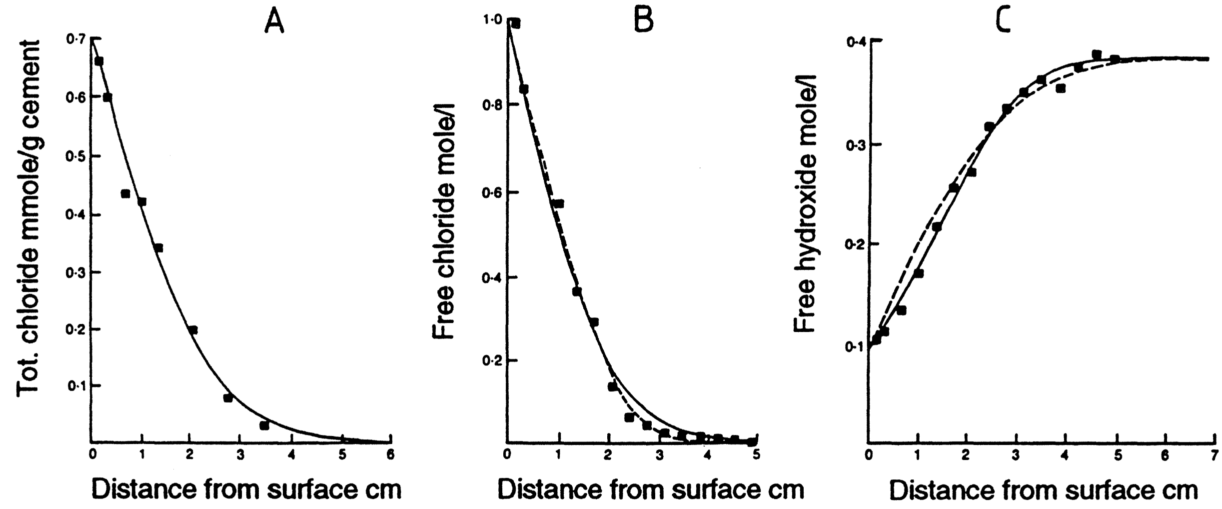


Fig. 22. Concentration profiles of total chlorides (A), dissolved chlorides (B) and dissolved hydroxides (C), for Portland cement paste of w/c 0.50 immersed for 100 days in a solution of 1.0 M sodium chloride saturated with calcium hydroxide /75/.

5.5 The effect of pozzolans and of the w/b ratio on the pore solution alkalinity

Pozzolans added to the concrete generally reduce the alkalinity of chloride free concrete, since alkali ions are removed from the pore solution as the pozzolanic reactions proceed /23,69/. The effect is illustrated using experimental data in Fig. 23, for concrete with silica fume in the binder fraction and paste, being membrane cured for about 6 months. Fig 23 also illustrates the effect of a decreased wet porosity caused by a decreased w/b ratio.

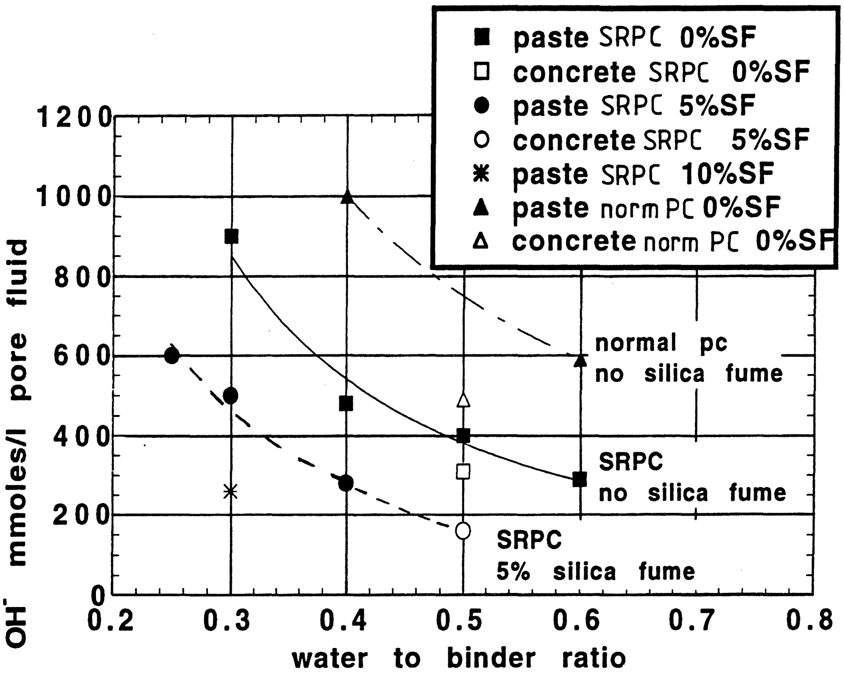


Fig. 23. The measured alkalinity in the pore solution of membrane cured cement paste and concrete made of various binders at various water to binder ratios /23/.

6 EFFECT OF SOME PROTECTIVE MEASURES ON THE CHLORIDE INDUCED REINFORCEMENT CORROSION

6.1 General

The effects of some protective measures aiming at improving the corrosion properties of the reinforcement in concrete are briefly discussed. The protective measures include organic and metal coating of reinforcement steel, corrosion inhibitors, non metal reinforcement, selective use of stainless steel and cathodic protection of steel. (Principles for repair of damaged concrete, such as electrochemical realkalisation, are not discussed.) Finally, a brief discussion of external coating of concrete is undertaken.

6.2 Organic coatings on reinforcement steel in concrete

Theoretically, steel coatings such as epoxy resins etc., may inhibit the transport of oxygen and/or aggressive ions to the coated naked steel /26,27/. In practice, however, several drawbacks must be considered such as:

A) The long term stability of epoxy resins is uncertain. Modern high quality concrete structures are today being designed for a calculated service life of more than hundred years. Little information exists on the very long term stability of epoxy and other types of organic coatings in very alkaline environment. It is known however, that many organic materials degrade and/or become very brittle within 10-50 years in alkaline environment such as in concrete. Thus, it is most uncertain if epoxy coatings will be efficient in blocking ion and/or oxygen transport more than 50 years after installation, i.e. the time period when its protective power would be needed.

B) Any crack in the protective coating would promote the development of severe pitting corrosion if chlorides and oxygen reach the crack. The corrosion rate in cracks would be controlled by the ability of the cracked epoxy coating to provide oxygen and electrolyte for the corrosion process.

C) Cathodic protection (if considered necessary at later ages due to incomplete function of the coating) would be much more complicated to install and operate /26/, since it requires metal connections to all steel considered for the cathodic protection. Therefore, the epoxy coating must be applied after preparing for cathodic protection. On the other hand, it is possible that an epoxi coating may reduce the current needed for a preventive cathodic protection.

6.3 Metal coatings on ordinary steel in concrete

Hot dipped zinc coated steel is the most commonly used metal coated reinforcement in concrete. A wide variety of zinc coated steels are available depending on the coating procedure and the composition of the ordinary steel, as reviewed by Sørensen /26/. Unlike ordinary steel, zinc passivates in carbonated concrete. However, when considering chloride initiated corrosion in uncarbonated concrete, the following drawbacks must be considered for zinc coated steel reinforcement:

A) The passivating properties of zinc in alkaline concrete are questionable. A field study of hot dipped zinc coated steel and normal ordinary steel in 20 years old submerged concrete in the sea indicated that the zinc coating was eliminated after 20 years of service. The original alkalinity of the concrete was calculated to pH 13.2, which decreased to pH 12.5. PH 12.5 is the buffering level of calcium hydroxide when alkali hydroxides have been leached totally.

Furthermore, little or no iron oxide was found on the steel, indicating an inhibited passivation of the ordinary steel due to the following factors: (i) black steel is cathodic as long as zinc is present, (ii) once all zinc was corroded, black steel turned anodic, but less oxygen was available to develop a passivating oxide layer on the steel /10/.

Most high quality concrete will for several decades remain alkaline within the range of pH 13.2 - 13.6 close to the reinforcement. Thus the zinc is likely to vanish completely long before it is supposed to protect the steel.

B) If zinc, in spite of the high pH, remains in metallic contact with the steel, it is uncertain if this type of cathodic protection will be sufficient to prevent pitting corrosion on the steel /26/. Probably it would be more efficient to use external zinc anodes exposed in sea water and being in metallic connection to the steel, if the purpose is to achieve cathodic protection of steel in concrete that is submerged or placed in the tidal zone.

C) The very low potentials of zinc coated steels will promote galvanic corrosion, if metallic connections are made with more noble metals in contact with oxygen. In alkaline concrete, ordinary steel is more noble than zinc. The effect is more pronounced in moist and chloride rich environments /26/.

D) The zinc coating may at least in theory cause debonding of reinforcement and embrittlement of steel, due to cathodic hydrogen evolution.

6.4 Corrosion inhibitors

Corrosion inhibitors decrease or eliminate the corrosion process by either inhibition of the cathodic reduction of oxygen or by inhibition of the anodic dissolution of iron. Chromium, nickel and other elements in stainless steel could in fact by analogy be regarded as anodic inhibitors, as they together with iron and oxygen form protective oxides immune to chlorides, thus preventing the chloride induced dissolution of iron. However, such a terminology is not used for stainless steels.

Several ions may in theory act in a similar manner, such as nitrites, being the most commonly used inhibiting additive in concrete /26/. As for ordinary steels coated with organic materials however, several drawbacks must be considered in long term field exposure. These are as follows:

A) Inhibitors added as an admixture to the fresh concrete are water soluble. For similar reasons as above, the long term function of soluble inhibitors is questionable. Any water soluble substance added to concrete will more or less be leached in any aggressive environment involving the transport of water. Thus, when chlorides eventually reach the steel, most rapidly via cracks and other heterogeneities in concrete, the soluble inhibitor will have been leached through the same transport channels as for the chloride ingress.

However, in very dry concrete such as the parking houses mentioned previously, soluble inhibitors may maintain long term effectiveness if capillary suction is the dominating transport mechanism for water in concrete.

B) Any local areas with incomplete function of the inhibitor, such as leached areas of cracks, may promote the development of severe pitting corrosion which is similar to what was the case for organic coatings, if the cathodic reaction is accelerated.

Nitrates in certain concentrations can be susceptible to accelerate the cathodic reactivity of steel. This phenomenon has apparently not been studied in practise /6/.

Bearing these considerations in mind, the inhibition effect of chromium, nickel and other elements in stainless steels appear more durable compared to soluble inhibitors added to the concrete. Furthermore, it should be noted that several inhibitors are toxic, thus being difficult to handle in practise.

6.5 Non-metallic reinforcement in concrete

Non-metallic reinforcement bars for concrete is available on the market. The most commonly used non metallic type of reinforcement is based on glass fibres in a matrix of polyester based polymers /26/. Its use in concrete has so far been very limited due to the following reasons, among others:

A) Similar to organic coatings, the long term stability of reinforcement based on organic material in alkaline concrete is uncertain.

B) The mechanical properties of existing non-metallic reinforcement are very different compared to steel. The modulus of elasticity is markedly lower compared to steel /26/.

C) The bond between non-metallic reinforcement and concrete is regarded less effective compared to the bond to steel.

6.6 Stainless steels in concrete

Several medium and high alloyed stainless steels are known to exhibit excellent resistance to chloride induced pitting corrosion, when used in the chemical industry. This is due to the formation of a more chloride resistant passivating oxide layer containing Cr_2O_3 and other more corrosion resistant oxides.

The schematic stability of a passivating layer containing Cr_2O_3 formed on chromium in a highly saline solution is shown in Fig. 24 /28/. Note the indicative nature of Fig. 24 with respect to stainless steels, due to the fact that iron is alloyed with chromium, nickel and other elements in stainless steel. The stability regions and oxide compositions for stainless steels in concrete with high chloride concentrations would therefore become different from what is shown in Fig. 24.

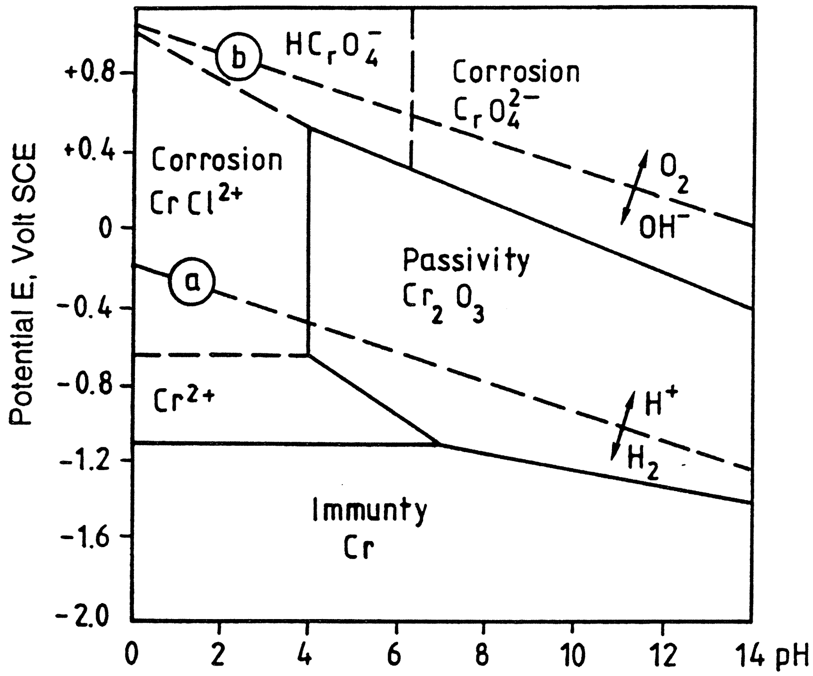


Fig. 24. Potential - pH diagram for chromium and chromium oxide in very saline brine (129 g Cl/litre) at 25°C /28/.

A wide variety of stainless steels exist on the market, from quite inexpensive low alloyed steels, being more sensitive to chloride induced pitting and welding corrosion, to expensive, but extremely resistant, high alloyed steels.

However, relatively high prices and little knowledge among civil engineers on the properties of stainless steels in concrete have so far limited its use to some very special applications, for instance concrete with restricted cover and exposed to severe environments.

Most stainless steels today used as reinforcement are of the austenitic type, associated with a 5-10 times higher tolerance for chlorides as compared to the ordinary steel used in concrete. But the less chloride resistant ferritic type of stainless steels have more similar mechanical properties as compared to ordinary steel. Therefore they are probably more suitable as partial replacement for ordinary steel in high quality concrete /26/.

In Table 2, critical chloride contents for stainless steel used as reinforcement in concrete are shown compared with the critical chloride content of black steel. The data have been evaluated from (i) Potentiostatic polarisation tests up to 200 mV SCE made by Sørensen, Jensen and Maahn /17/, (ii) 10 years outdoor atmospheric exposure tests made by Treadaway, Cox and Brown /117/.

Note that the given data cannot directly be used for service life prediction, since the data was derived from concrete with cast-in chloride, without any knowledge of the concentration of free chloride and hydroxide. In the study by Treadaway /117/ the potentials were not reported.

However, the data is illustrative and can be used as a relative indication of the chloride tolerance for stainless steels as compared to ordinary steel in concrete.

Table 2. Relative critical chloride concentrations for various stainless steels in concrete as compared to ordinary steel. Data derived from /17,117/.

Ref.	Type of steel (AISI no)	Chemical composition %	Approx. critical Cl content, % by weight of cement	Rel. improvement as compared to ordinary steel
/117/	405 ferritic	13Cr 0.07Ni 0.09Mo 0.36Mn	1.0	more than 2 times
/117/	430 ferritic	17Cr 0.18Ni 0.17Mo 0.39Mn	1.9	more than 4 times
/117/	302 austen.	18Cr 8.8Ni 0.18Mo 0.78Mn	1.0-1.9	more than 2 times
/17/	304 austen.	18Cr 8Ni	3.5-5.0	more than 8 times
/17/	welded 304	18Cr 8Ni	1.0-2.0	more than 2 times
/117/	315 austen.	17Cr 10.1Ni 1.4Mo 1.6Mn	> 3.2	more than 8 times
/17/	316 austen.	18Cr 10Ni 2Mo	3.5-5.0	more than 8 times
/17/	welded 316	18Cr 10Ni 2Mo	1.0-2.0	more than 2 times
/117/	316 austen.	17Cr 12Ni 2.1Mo 1.9Mn	> 3.2	more than 8 times
/17/	ordinary steel		<0.5, approx. 0.4 assumed	
/117/	ordinary steel		>0.3, approx. 0.4 assumed	

As reported by Treadaway et. al. /117/, the ferritic types of stainless steel are less chloride resistant as compared to the austenitic types. But still the former are much more chloride resistant as compared to ordinary steel, thus in many cases being a cheaper, but good enough, alternative for the use with high quality concrete.

Generally, little field experience has yet been reported on the performance of stainless steel in concrete, probably because of a satisfactory performance.

More systematic field and laboratory studies would be needed in order to evaluate the most cost effective choice of stainless steel as partly replacement of ordinary steel reinforcement in concrete exposed in the most aggressive environments.

The selective use of stainless steel of moderate quality in some most critical exposure zones, as illustrated in Fig. 25, may considerably improve the service life of a structure at a reasonable additional cost.

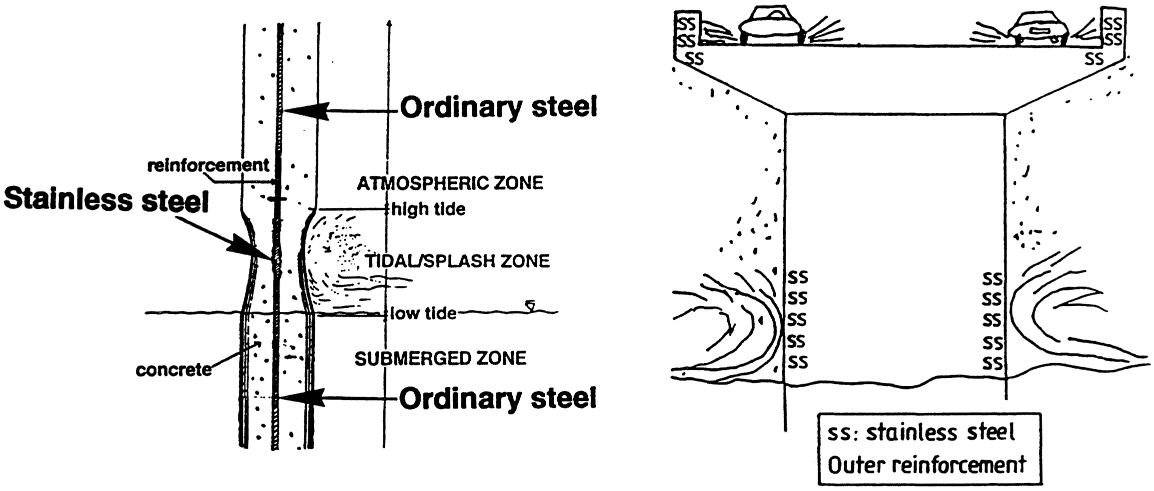


Fig. 25. (A): One possible design for a selective use of stainless steel in concrete exposed for chlorides in the aggressive splash zone of a marine exposed column. (B): Some very aggressive zones indicating possible selective use of stainless steel reinforcement.

6.7 A discussion of some corrosion properties of stainless steel in concrete in galvanic contact with black steel.

Stainless steels and ordinary steel passivate in alkaline concrete at very similar steel potentials. Besides, the cathodic reaction is inhibited on stainless steel as compared to the cathodic reaction on ordinary steel, if connected to a corroding ordinary steel /26/.

As a consequence, connections between stainless steel and ordinary steel will not promote galvanic corrosion any more than do connections between ordinary steel and ordinary steel.

The gradients in potential developed in a given concrete structure with stainless steel connected to ordinary steel will therefore not become any greater as compared to what is the case at the present use of solely ordinary steel.

As indicated in Table 2, most stainless steels loose some of their immunity for corrosion if welded. The amount of loss in immunity depends on the alloy composition and the welding technique. However, several laboratory investigations and some field experience regarding the use of welded stainless steels in concrete have indicated a dramatically increased tolerance for chlorides compared to the conventionally used steel /17,26/.

Any corrosion attack on combined ordinary steel - stainless steel reinforcement would initiate on the ordinary steel, because of its lower resistance to chlorides. Such an attack would, however, not become an accelerated "galvanic" attack, since the cathodic reaction rate is inhibited on stainless steels as described above.

Thus, the combined use of ordinary steel - stainless steel reinforcement when in metallic connection with each other will not result in any negative corrosion properties; nor for the ordinary steel, neither for the stainless steel.

However, stainless steel in welded connection with stainless steel will be more susceptible for pitting corrosion at the weld as compared to the unwelded stainless steel. Stainless steel in welded connection with ordinary steel, on the other hand, will always act as a cathode, thus being very well protected by the ordinary steel.

The questions to be answered are (i) which types of stainless steels, and (ii) which kind of joint for stainless to stainless steel, that would be preferable with respect to corrosion properties, mechanical properties and economy.

Provided that the stainless steel considered is used in a high quality concrete structure, being durable to other types of environmental attack, also the more inexpensive types of stainless steel available are likely to perform well enough to ensure corrosion initiation times well exceeding 100 years, as exemplified in Chapter 9. Furthermore, a reduced cover thickness may be tolerated as calculated in the same chapter.

6.8 Cathodic protection of steel in concrete

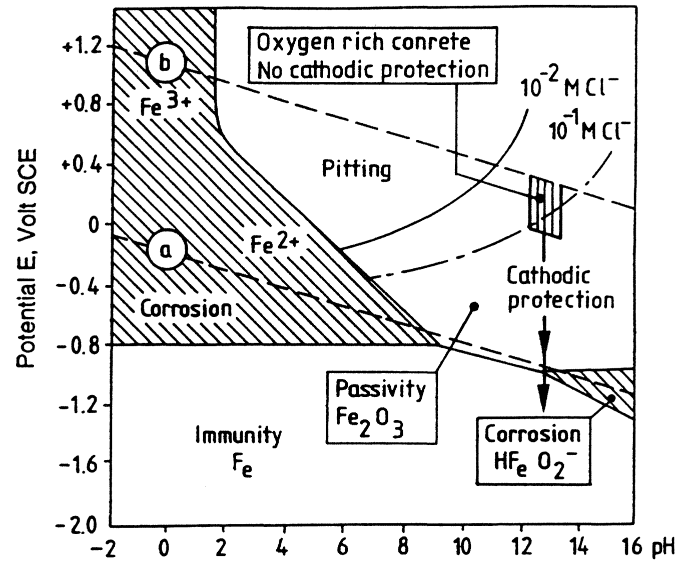


Fig. 26. Cathodic protection of iron or steel as illustrated by a potential drop in a potential - pH diagram /18/.

Cathodic protection of any metal in any environment involves a depression of the metal potential down to a potential which makes the anodic dissolution of the metal impossible, as illustrated in Fig. 26. As indicated, anodic dissolution is impossible, in alkaline solution below the equilibrium potential for hydrogen evolution /18,21/.

Considering steel in concrete, a partial cathodic protection will in most cases be sufficient but less costly as compared to the complete cathodic protection shown in Fig. 26. Partial cathodic protection occurs when the steel potential is not depressed all the way down to the corrosion immunity region. However, the steel potential must be low enough to avoid pitting corrosion and to maintain a very low corrosion rate.

A partial cathodic protection is sometimes desired since any negative effects possibly associated with hydrogen evolution, such as debonding or hydrogen brittleness of the steel, can be avoided. Furthernore, a partial cathodic protection installed before the development of pitting corrosion is less costly to maintain as compared to cathodic protection executed after the initiation of pitting corrosion.

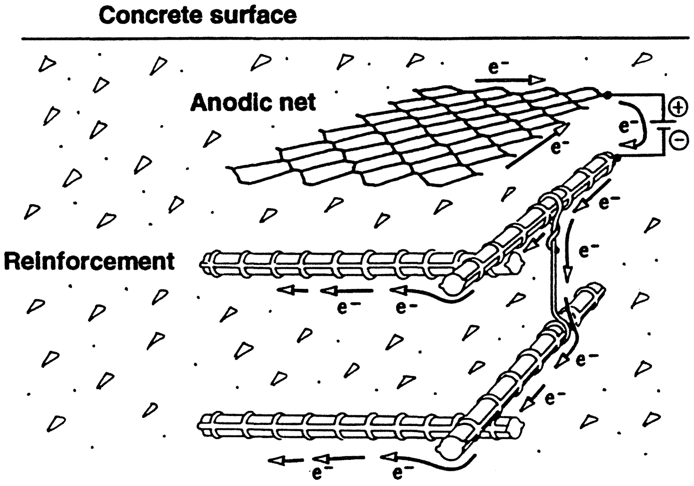


Fig. 27. Illustration of cathodic protection of reinforcing steel in concrete /18/.

Cathodic protection is quite easy to install and operate on steel in water saturated concrete. Such concrete has a relatively low resistivity, making it easy to regulate a protective flow of electrons from an external or internal anode to the cathodic reinforcement, as illustrated i Fig. 27 /18/. The anode used for water saturated concrete may be either inert, connected to an external current, or a sacrificial external anode of corroding metal.

Cathodic protection becomes more complicated to install and operate on steel in semi dry concrete. Large variations in concrete resistivity due to moisture gradients make it difficult to establish an uniform current from steel to anode protecting all parts of the steel. Because of a higher concrete resistivity, inert anodes must be placed quite close to the reinforcement supposed to be cathodically protected.

A more efficient inert anodic net is indicated in Fig. 27, to be cast into concrete. Such anodic nets have been developed in recent years, as well as anodic paints to be applied to the concrete surface. The durability of such anodic systems is uncertain. The design life is probably 10-20 years /26/. Sacrificial anodes are usually not sufficient for steel protection in semi dry concrete. However, sacrificial anodes have been operating successfully at a floating concrete bridge in Norway for several years, apparently bringing the steel potential below the pitting potential /29/.

Such cathodic protection by sacrificial anodes for wet concrete is more or less self-regulating, since it is controlled by the corrosion rate of the sacrificial anodes. No active control system is necessary provided that the concrete is wet enough to maintain the desired, low steel potential. However, the electrolyte between the anode and the concrete must be saline enough to ensure good conductivity.

Cathodic protection using external currents on the other hand needs more complicated systems for an active control of the output current. Especially for semi dry concrete, it is sometimes difficult to achieve suitable potentials and currents through a reinforcing system involving several exposure zones. Control systems and -criteria for various exposure conditions are under development /30/.

6.9 External coatings on concrete

Various principles for external surface coatings on concrete are commercially available. The coatings aim at substantially reducing the surface chloride permeability of the concrete as compared to the uncoated concrete /118/. A concrete coating may be regarded as beneficial as compared to a reinforcement coating, since the concrete coating would block the chloride transport almost immediately after application. A reinforcement cover, however, would not block any chloride transport until the chlorides have reached the reinforcement, i.e. after several decades when considering a modern, high quality construction.

However, most coatings probably have a short service life on a 100 years time scale. Furthermore, several of the most efficient polyurethane based coatings must be applied on a carbonated concrete surface, since the polymer is not durable in alkaline environment.

A very beneficial application of early surface coating is under development using alkali resistant polyurethane. Thus, the coating could be applied a few days after concrete casting, and therefore allowing early exposure of the structure without any rapid early chloride ingress into the concrete. The benefit from such a measure may be significant even if the service life of the coating is only a few years /119/, provided that no negative effects, such as a reduced resistance of the concrete surface to freezing and thawing, are introduced.

Another beneficial system for surface protection of concrete is illustrated in Fig. 28. If not removed after casting, the form work may act as a barrier in some most critical exposure zones. If the barrier is made of stainless steel, the barrier could be cathodically protected to some extent by a metallic connection to ordinary steel reinforcement at a very low potential /6/.

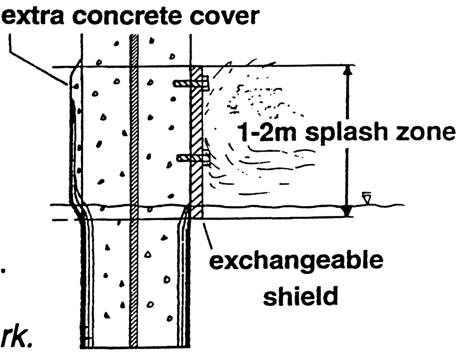


Fig. 28. Surface protection f.i. by a remaining form work.

7. DEGRADATION OF POROUS MATERIALS

7.1 General

In this chapter a general discussion is undertaken on the degradation process of porous materials such as concrete in aggressive media. The discussion will later in this chapter serve as a background when discussing chloride transport in concrete long term exposed in various aggressive environments.

On the geological time scale all materials are more or less unstable. Concrete is an unstable material when compared to some natural materials such as quartz rock, though concrete is a very stable material compared to most man made or organic materials.

In Fig. 29 /33/, concrete would be found somewhere in the upper right part when placed in a geological stability series. Other building materials such as steel, wood and most plastics would be found above concrete, thus being less stable.

wood
plastic
ordinary steel
Olivine Calci-plagioclase
Augite Calci-alkali-plagioclase
Concrete
Hornblende Alkali-calci-plagioclase
Biotite Alkali-plagioclase
Orthoclase (potash feldspar)
Muscovite
Quartz

Fig. 29. Browns geological reaction series. Each mineral is more stable than the one above it on the list /33/. Concrete would fit somewhere in the upper right corner if compared to the minerals on the list, being more stable compared to wood, steel, plastics, etc.

Nearly all construction materials thus have a driving force to degrade. Some construction materials are so unstable that they disintegrate without any external action, no "activation energy" is needed.

Some plastic materials and some aluminate cement concrete mixes degrade at room temperature without any external action.

The conversion of beta-tin (high density) to alpha-tin (low density) below 13°C eventually resulting in pulverisation of the material, tin pest /34/, is a classic example of spontaneous degradation of an unstable material.

The degradation rate of any reasonable stable material depends on the ability of external forces to execute the degradation. Climatic aggressiveness and the permeability of the material are the key factors controlling the rate.

7.2 Climatic aggressiveness

Most physical and chemical degradation processes involve the transport of water and salts. Although cyclic thermal expansion and contraction by itself causes stresses and cracking, for instance in vacuum environment on the moon, the effect is for most materials very much accelerated in the presence of water and salts. New surfaces formed by expansion - contraction cycles adsorb and react with water, resulting in dissolution and weakening of the material in the newly exposed surface /33/.

The process of water reaction and weakening of the material will not continue in the presence of static water. Continued driving of the reaction requires removal of soluble materials by leaching, complexing, adsorption, or precipitation. The pH of the system is very important, since it affects the solubility of the attacked material and the precipitation (if any) of protective solids decreasing the mobility of water, i.e. self healing /33/. Note the analogy with ordinary steel in alkaline water, where a protective solid, the oxide layer, prevents further dissolution of the steel.

Crystal growth and frost action are two of the most powerful mechanisms for the degradation of porous materials in contact with water. Although the mechanisms of degradation are not fully understood, some striking similarities exist when comparing the action of some types of crystal growth with frost action on porous materials /35-37/. Both degradation types become most powerful at cyclic temperature variations on water saturated materials unable to accommodate the hydraulic pressure introduced when water and/or dissolved salts solidify. A properly sized and distributed air void system will, if not water saturated, release the hydraulic pressure and thus significantly delay or completely hinder the attack.

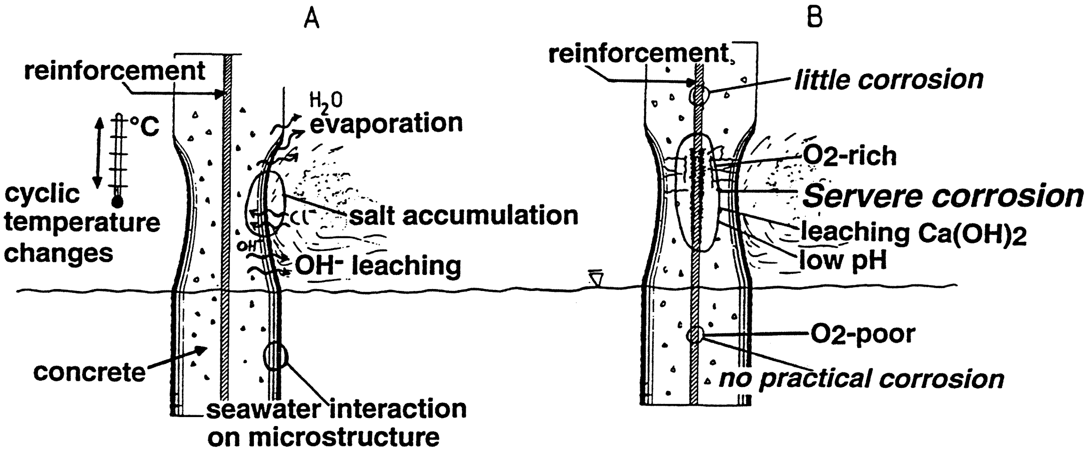


Fig. 30. Schematic illustration of some mechanisms of degradation for a marine concrete structure. (A): Frost and chemical attack on a marine concrete. (B): Reinforcement corrosion in humid concrete.

A temperature increase accelerates most degradation processes, unless the mechanism is based on cycling temperatures or on reaction in a specific temperature range. As a rule of thumb, a temperature increase of 10 °C will double the rate of most chemical reactions.

Temperature cycles have a very strong effect on moisture transport. The drying shrinkage of hydrated materials such as concrete may cause significant tensile stresses and cracking. As the shrinkage is influenced by the moisture state, which in turn is influenced by the temperature, cyclic drying shrinkage - swelling may develop due to cyclic changes in both temperature and the moisture state.

In Fig. 30, some mechanisms of degradation are illustrated for a marine concrete structure. As indicated, the environmental action on porous materials vary extensively depending on local exposure conditions. Thus, chloride profiles and chloride penetration depths may vary significantly when analysing concrete samples taken from various positions on structure.

7.3 Permeability of concrete

7.3.1 General

In a given exposure condition, the long term permeability of the concrete will decide the rate of degradation, as illustrated by Mehta in Fig. 31 /45/. Most degradation processes are initiated and/or accelerated by the formation of cracks and the interconnection of cracks and voids that are frequently found in field exposed concrete structures.

Open cracks act as effective paths for water, oxygen and dissolved ions, thus exposing new surfaces to the degradation forces. Heterogeneities such as a more porous transition zone between the paste and the aggregate, compaction pores, etc., may originally be isolated and become interconnected to crack systems, thus increasing the long term permeability.

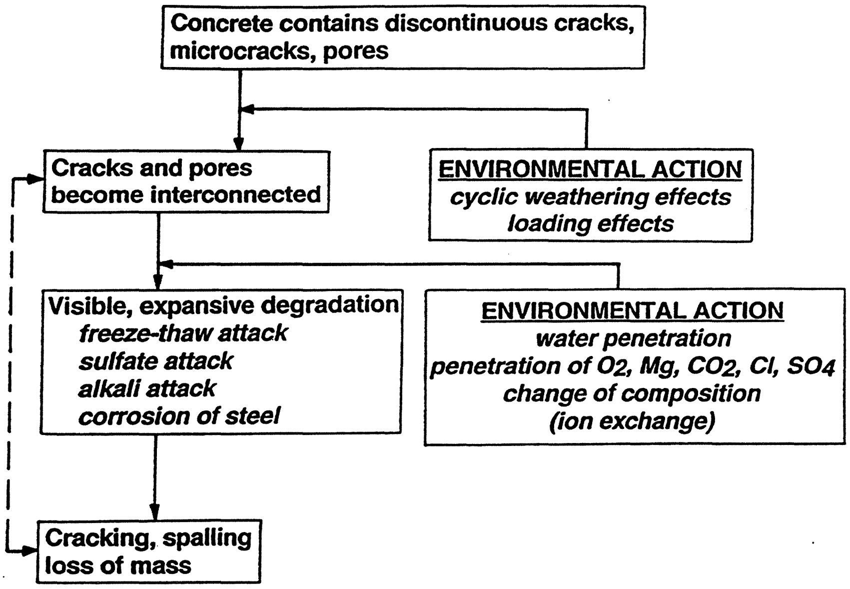


Fig. 31. A holistic model of the deterioration of originally very water-tight concrete as influenced by various environmental effects /45/.

7.3.2 Chloride permeability of concrete

Fig. 32 illustrates the general relationship between the chloride diffusivity and the water to binder ratio for normal concrete /47,48/. The water to binder ratio reflects a more fundamental relationship between porosity distribution and permeability. Especially for dense concrete with almost zero initial permeability, the effects of the formation and the inter-connection of cracks may be dramatic.

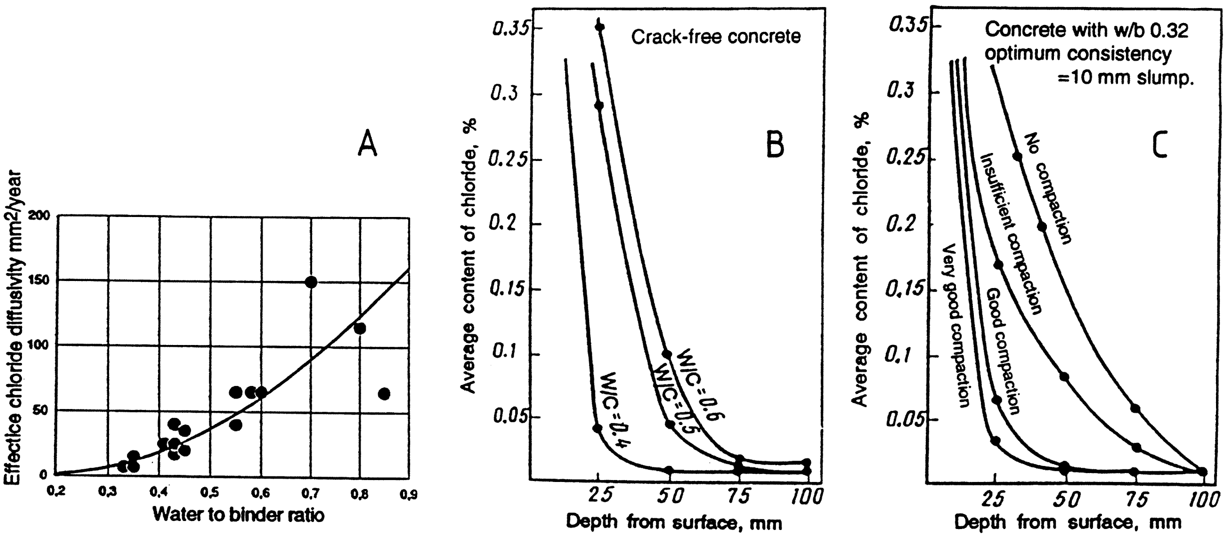


Fig. 32. (A,B): General relationship between the chloride diffusivity and the water to binder ratio as measured on drilled cores from existing concrete structures. (C): The effect of insufficient compaction on chloride permeability for concrete /47,48/. In (B,C) the chloride profiles were measured after 830 days exposure to salts.

7.3.3 The effect of varying climatic aggressiveness on chloride penetration in concrete

Fig. 33 illustrates the micro environmental influence on the chloride profiles after 4 years of field exposure, at various sampling positions at the same side of a single marine concrete column at the New Öland bridge, which is situated in the Baltic Sea, Sweden. The concrete used was a very uniform, high quality air-entrained concrete with a water to binder ratio < 0.40. /31,50/.

Note that a system of cathodic protection has been operated on the concrete column studied. The electrical field developed in the system is likely to have affected the chloride penetration to some extent. However, the effect of the cathodic protection is not likely to have significantly affected the general spread between chloride profiles found at various exposure zones. A similar general relationship between the measured chloride profiles and the sampling distance from the sea water level has been found on several marine structures not being cathodically protected, for instance as reported by Fluge and Blankvoll /126/.

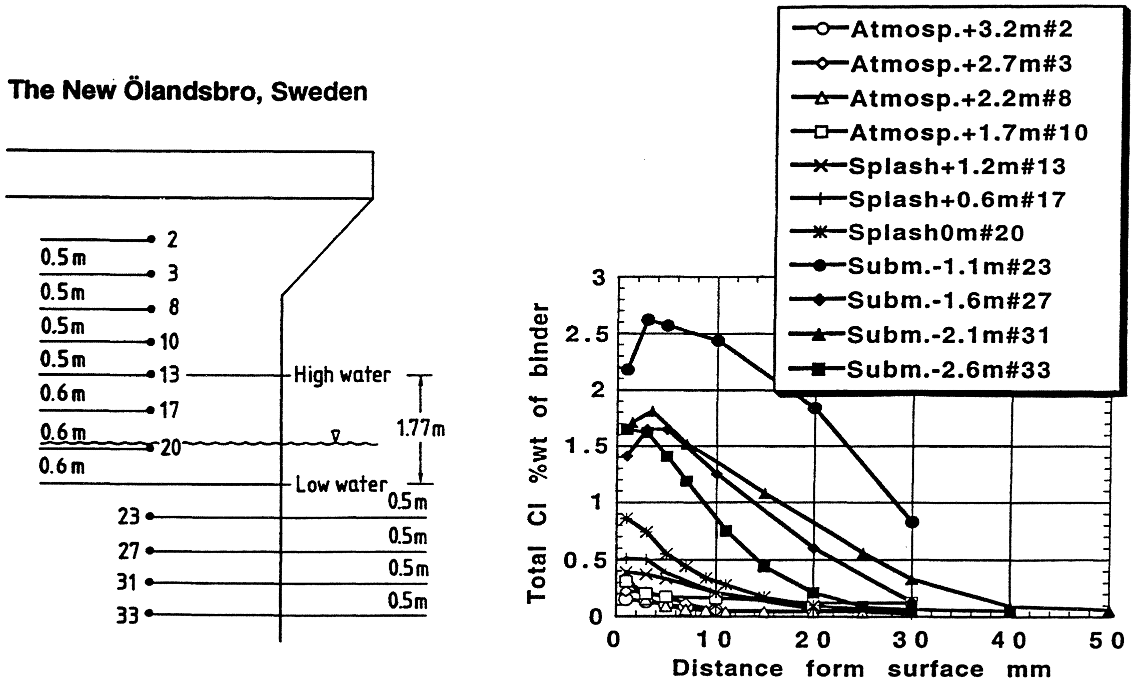


Fig. 33. The effect of the micro environment on the chloride penetration in a high performance concrete at various heights from the mean water level. The chloride profiles were analyzed on concrete cores drilled after 4 years of exposure /31,50/.

A recent field study of 8 concrete bridges exposed 2 - 40 years in marine environment in Norway indicated large variations in the chloride penetration at various positions on single bridges. The variations in "effective chloride diffusivity", calculated applying Fick's second law of diffusion for the measured chloride profiles, were larger at various positions on a given bridge than when comparing bridges at various locations at the Norwegian coastline /51/.

Similar findings have been reported by the Danish Road Directorate /52/, regarding a large field investigation of 20 concrete bridges exposed for chlorides from deicing salts and/or from the sea.

These findings are very similar to the results from field studies made on ancient churches, monuments, etc. /53/, of the varying aggressiveness of the micro climate. Apparently, the time of wetness plays a significant role in controlling the degradation rate, thus indicating some similarities in degradation of rocks and degradation of concrete. However, the time scale and the specific mechanisms of degradation are in several cases different.

7.3.4 A discussion of the interpretation of concrete permeability data

The significance of concrete permeability as regards durability is not univocal in the concrete literature. Several researchers claim that a very low permeability measured on a more or less ideal laboratory specimen would indicate a very long service life of a field exposed structure made of a similar material. However, a very dense and very low permeable concrete is usually also very brittle, making it sensitive to various internal and environmental loads.

A classic example is a 100x200 mm paste cylinder made of macro defect free cement "Densit" at a very low water to binder ratio. Such a paste is associated with an extremely low chloride permeability measured on virgin specimens, but it has been reported to disintegrate when stored in at room temperature /46/, probably due to internal stresses caused by self dessication and moderate drying. Densit must therefore usually be reinforced by fibres in various ways depending on its application.

It is therefore very important to recognise that it is the long term permeability over the entire service life which controls the degradation curve of a given structure. The long term permeability is largely dependent on local exposure conditions, modifying the concrete micro structure over the years /31/. This long term permeability for a given concrete quality has often very little to do with the original chloride permeability as measured on laboratory-made concrete after 28 days of standard curing.

The role of calcium hydroxide in concrete is also sometimes under debate. It may be argued that large crystals of calcium hydroxide serve as weak spots in the concrete matrix /25/. When calcium hydroxide is dissolved, remaining voids would contribute to a higher permeability.

On the other hand, the calcium hydroxide contributes strongly to the self sealing mechanism of concrete /10,31,39,40,41/, as discussed more in detail later. Furthermore, the presence of calcium hydroxide will provide a minimum level of alkalinity (pH > 12.4), thus maintaining a certain tolerance for chlorides at the reinforcement as previously discussed /13,30/.

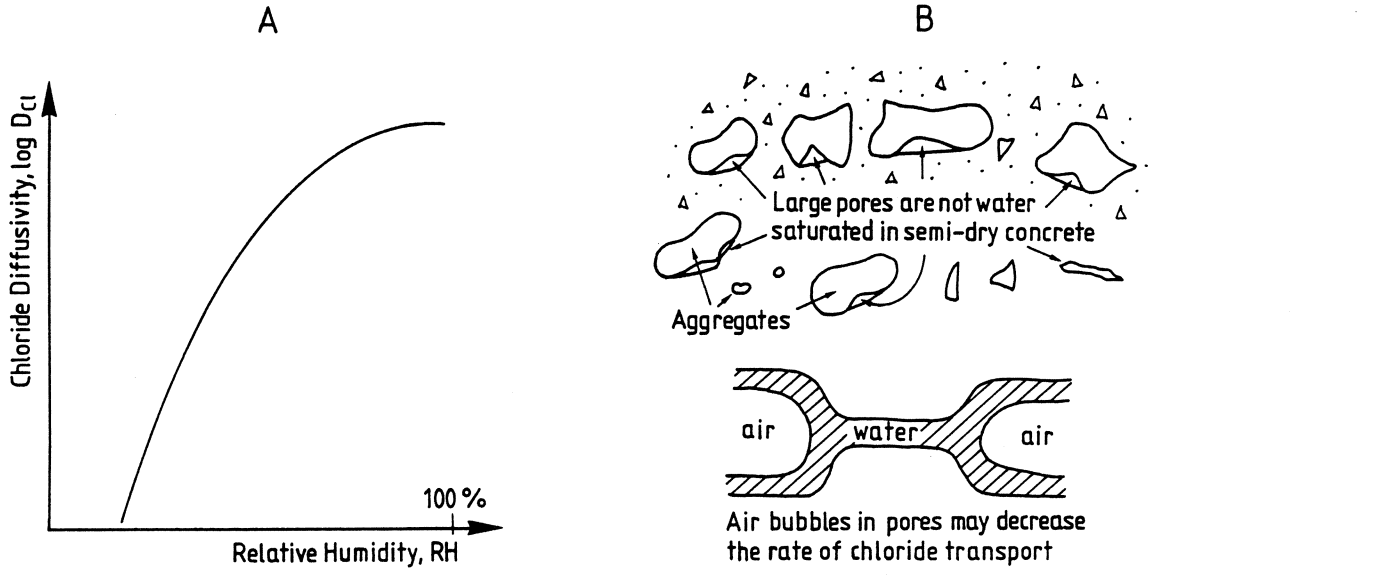


Fig. 34. (A): Expected relationship between the chloride permeability and the moisture state for a given concrete. (B): Partly saturated concrete pores reducing the chloride transport rate /37,49/.

The concrete permeability for chlorides and other water dissolved ions is usually measured on water saturated specimens. However, most high quality concrete exposed to the atmosphere are not water saturated. Since chlorides are transported being dissolved in water, a relationship between the chloride permeability and the concrete moisture state as illustrated in Fig. 34 is expected.

The relationship between the gas permeability and the moisture state of concrete is more or less opposite to that shown in Fig. 34 (A), as illustrated by Tuutti in Fig. 17, which is valid for oxygen /8/.

At present few data exist on chloride transport in semi-dry concrete. A reduced rate of chloride permeation in semi-dry concrete is probably one important reason for many observations of marked reductions in the chloride penetration rate in concrete over time /31,42/. Thus, the "effective chloride diffusivity" is reduced with the time of exposure.

On the other hand, dry cracks and dry capillary pores connected to the concrete surface are rapidly rewetted by capillary suction if exposed to liquid water /49/. Thus, a cracked concrete or a concrete with high water to binder ratio will facilitate rapid oxygen and chloride transport if subjected to cyclic wetting and drying in a saline environment. A general theory on the interrelationships for transport of moisture, water, gases and ions in concrete has been discussed by Nilsson and Tang /49/.

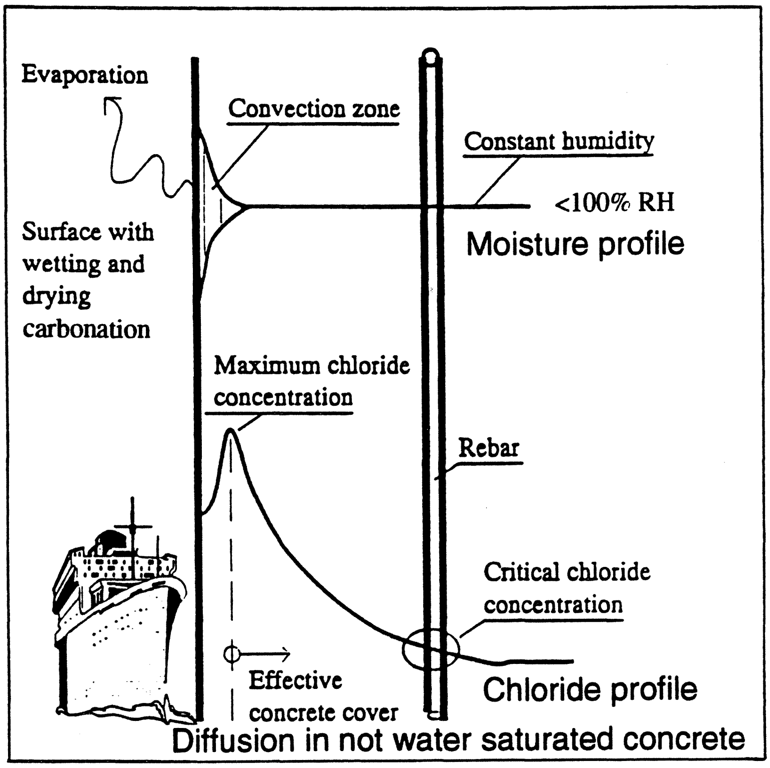


Fig. 35. Schematic illustration of the moisture and chloride profile in a high quality concrete, as a result of environmental action and self dessication of the binder. Moisture gradients give rise to other chloride transport mechanisms than diffusion, such as convection. Chloride diffusion in the semi-dry bulk concrete is therefore not equivalent to diffusion in water saturated concrete /19/.

7.3.5 Representing chloride permeability by Fick´s second law of diffusion

Fick´s second law of diffusion is widely used to predict the long term chloride transport into concrete exposed in the splash- and the atmospheric exposure zone. The use of a diffusion law for describing the chloride transport into concrete that is exposed to frequent cycles of wetting and drying is probably not scientifically correct, as illustrated in Fig. 35 /19/.

Cracking, drying and wetting, wave action, etc. results to some extent in chloride transport due to capillary suction and permeation by over-pressure. However, for high quality concrete, in most practical cases, these transport mechanisms result in quite similar chloride profiles as for diffusion, providing that the concrete is not seriously degraded or that the exposure conditions are not too extreme /51,52/.

Therefore, from an engineering point of view, it seems quite possible to describe the long term chloride penetration into the concrete using a modified version of Fick´s second law of diffusion /54,55/. Any changes in the concrete micro structure and the moisture state, as influenced by drying, leaching, cracking, etc., result in changes in the porosity, the degree of saturation, the chloride binding, etc. These changes can be accounted for by a variable "effective chloride diffusivity" which may vary both with respect to time and concrete depth.

In Fig. 36, an example is given on the time dependency of the effective chloride diffusivity for submerged concrete, as calculated from the total chloride profiles at various exposure times using Fick´s second law of diffusion.

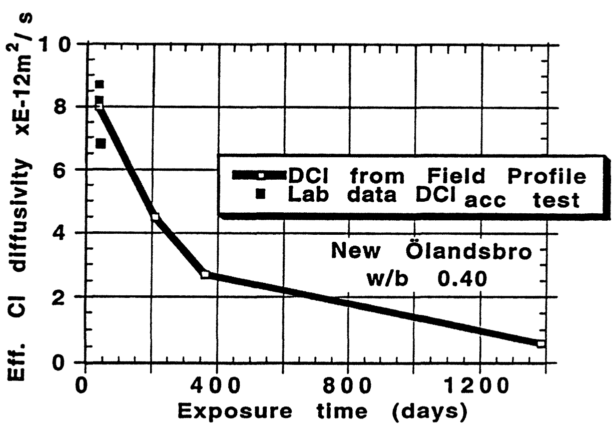


Fig. 36. Effective chloride diffusivity for submerged concrete as calculated from total chloride profiles using Fick´s second law of diffusion at various exposure times /31/.

The dynamic effects of environmental action, such as drying, leaching, cracking, etc., can be monitored for a given concrete type in a given environment /54,57/.

However, for concrete subjected to capillary suction, with high water to binder ratio, or subjected to extensive cracking, the resulting chloride profile may be quite different from that predicted by Fick´s second law of diffusion /58/. Under these circumstances it becomes very difficult to evaluate the chloride transport in terms of an effective chloride diffusivity as discussed by Janz and Johannesson in /58/.

Attempts have also been made to establish more scientifically based models for long term chloride transport in concrete as influenced by defects in the concrete micro structure as well as by the dynamic environmental action on concrete /55,56/. The numerical model outlined in /55/ is based on a variable chloride binding capacity, thus affecting the diffusion coefficient used in the modelling of the chloride transport. The variable chloride binding capacity is affected by changes in surface chloride concentration, temperature, degree of hydration, pore content and binder content. In this way the chloride diffusivity can be described as a function of depth, age and temperature /55/. The model described in /56/ is based on the simultaneous transport of chloride and moisture in concrete.

Apparently none of these models at present consider the effect of hydroxide removal and surface densification, although these factors easily could be accounted for numerically in the model presented in /55/. Data on the relationship between the chloride binding and the alkalinity of the pore solution is available in /69,71/. Some data on the relationship between the effect of sea water interaction with concrete and the capillary porosity as a function of depth, age and exposure conditions are available in /21,39,59,66/.

7.3.6 Predictions of the chloride penetration based on field data

As previously discussed, laboratory estimations of chloride penetration rates in concrete can never directly be used for the prediction of the chloride transport in field concrete. Such laboratory data need careful calibration against long term field observations, taking the long term effects of environmental interaction, cracks, etc. into account.

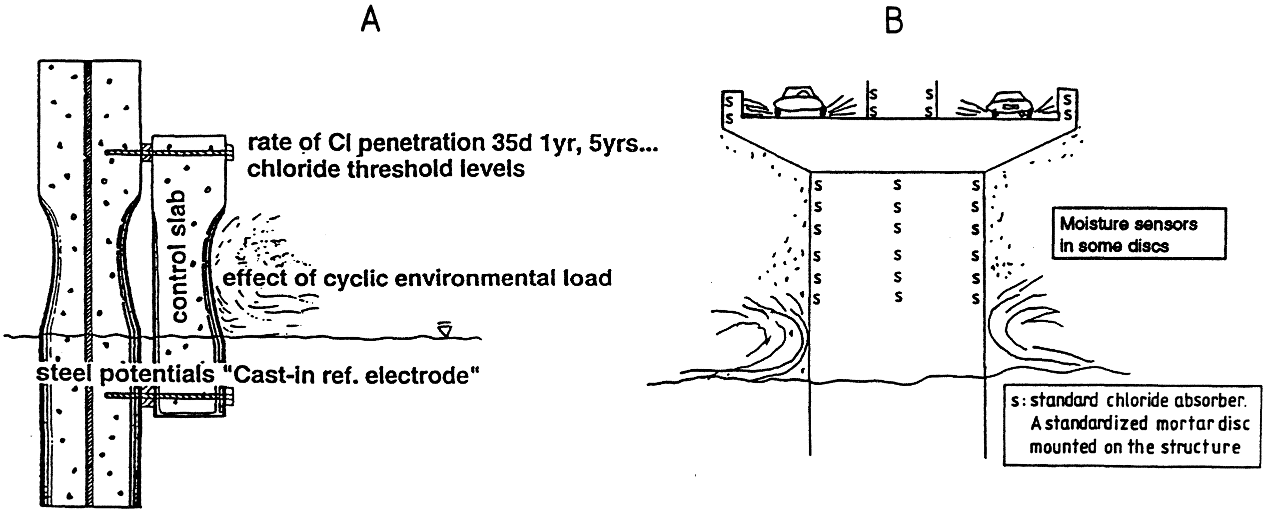


Fig. 37. Two systems for the systematic collection of field exposure data for concrete structures. (A): Control slabs being as identical as the parent structure as possible. (B): "Standard chloride absorbers" for a standardised evaluation of the relative aggressiveness of various micro environments with respect to chloride exposure.

A systematic approach of collecting various field data as a basis for service life prediction of reinforced concrete structures exposed in various micro environments has been suggested /57/. If a general procedure for collecting field data from various concrete types at various exposure conditions and ages could be agreed upon, it would be possible to establish data banks of relevant field concrete data for future predictions of concrete durability.

As shown in Fig. 37, concrete control slabs large enough to reflect a field structure, could be cast and placed parallel to the structure in some of the most aggressive exposure zones. In order to provide reliable field data for future repair needs and maintenance of the structure, the material and the design of such concrete slabs should reflect real structures. In addition, small standardised mortars, "standard chloride absorbers", could be placed on any structure for the purpose of identifying the relative aggressiveness of various micro environments with respect to moisture and chloride exposure.

7.3.7 Hydroxide ion permeability of concrete

As discussed previously, the alkalinity of concrete pore solution in contact with the steel affects the critical chloride concentration for initiation of active reinforcement corrosion. The alkalinity of a concrete pore solution varies significantly over time due to carbonation, leaching etc. Alkali hydroxides are highly soluble and thus strongly affect the alkalinity as expressed by the pH value.

Little quantitative data exist regarding transport coefficients for hydroxide ions in concrete. However, as discussed in chapter 5, it has been found that the hydroxide permeability generally is in the same order as the chloride permeability /22,75,120/.

In normal concrete, the amount of alkali hydroxide produced is less than 5 % of the amount of less soluble calcium hydroxide produced. Thus, as hydroxides are leaving field exposed concrete, pH approaches the buffer level of calcium hydroxide, approximately pH 12.4-12.5.

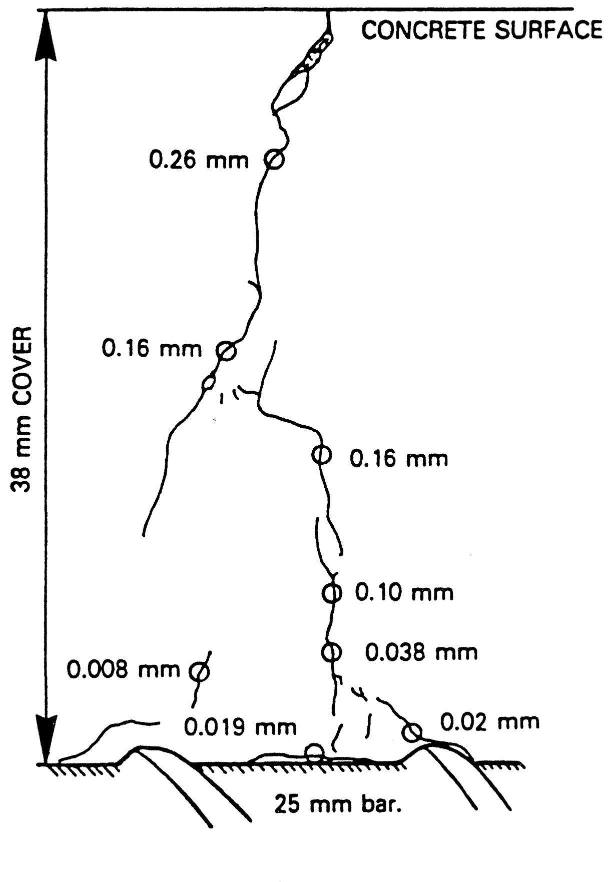
Therefore, for high quality concrete it is on the safe side to assume a long term alkalinity of pH 12.4 - 12.5 at the reinforcement at the time for corrosion initiation. Alternatively, estimations of the long term alkalinity at the reinforcement can be done assuming that the predicted coefficient for chloride transport can be used also to predict the hydroxide leaching, as illustrated in /75/. Such an approach will often result in a higher alkalinity than pH 12.5, especially if a high performance concrete exposed to the atmosphere is considered, since such a concrete probably will contain substantial amounts of unreacted cement also after very long exposure times.

7.4 Effect of cracks in concrete

7.4.1 General

As generally described by Mitchell regarding the degradation of porous rocks in /33/, the process of dissolution and weakening of the material will not continue in the presence of static water. Thus, a given crack in concrete may be harmless when filled with static water, such as in submerged concrete. On the other hand the same crack may be accelerating the degradation rate if water is frequently percolating the crack, such as in dried out and rewetted concrete exposed to the atmosphere /10/.

A typical crack system with a surface crack width of approximate 0.3 mm is illustrated in Fig. 38 /40/. The effect of a crack in the concrete will depend mainly on its capability to transport water and oxygen into the concrete over time, a property which in turn depends mainly on the exposure conditions and the self healing capacity of the binder. Critical crack sizes for concrete must therefore vary depending on exposure conditions and self healing capacity of the binder.



Reinforcement

Fig. 38. Example of geometric characteristics of a thermal crack system with a surface crack width of approximately 0.3 mm /40/.

In general, cracks in concrete may have the following negative effects on steel in the concrete:

A) Reducing the effective distance for chlorides, moisture and oxygen to reach the steel surface.

B) Formation of a corrosion macro-cell if the steel is depassivated, due to the fact that cracks give rise to low resistivity and to rapid ion transport from anode - cathode pairs separated a long distance from each other.

C) Accumulation of salts, if water evaporates in the crack. This may result in a differential concentration corrosion cell (pitting corrosion), since depassivated areas of steel below chloride rich cracks will be surrounded by passive steel.

D) Formation of an differential oxygen concentration cell, if oxygen is more easily available in the crack than in the surrounding wet concrete Then there is a cathodic action of the steel inside the crack.

E) Formation of a differential alkalinity cell, if the alkalinity at the steel close to a crack is locally changed compared to the surrounding concrete.

A-B) result in an overall decrease in resistance to reinforcement corrosion.

C-E) result in localised pitting corrosion, due to the formation of a galvanic type of corrosion cell. The micro environment within the crack affects the micro environment at the steel. Thus the steel potential close to the crack will shift compared to the steel potential in the surrounding crack free concrete.

The effects are generally accelerated by a wider crack opening and retarded by a thicker cover. As reported by Moskvin /21/, Alekseev /48/ and Schiessl /60/, the formation of a differential aeration cell (D) is not likely to occur in either submerged concrete, due to restricted oxygen permeability in completely wet cracks, or in dry atmospheric concrete, due to a general high availability of oxygen.

7.4.2 Self healing effect of concrete

The self healing, or sometimes referred to as crack sealing, capacity of concrete is probably similar to the self sealing effect of concrete permeated by water, as studied by Hearn /38/. She found dissolution of calcium, sodium and potassium followed by precipitation of solids containing these species to be the main mechanism behind self sealing. When performing water permeability tests, the permeability decreases sometimes several orders of magnitudes due to self sealing /38/.

The self sealing effect is even more pronounced when carbonates and magnesium from sea water combine with mainly calcium and hydroxide ions to form dense precipitates containing magnesium hydroxide and calcium carbonate /10,31,39,40,41,59/, see Fig. 39.

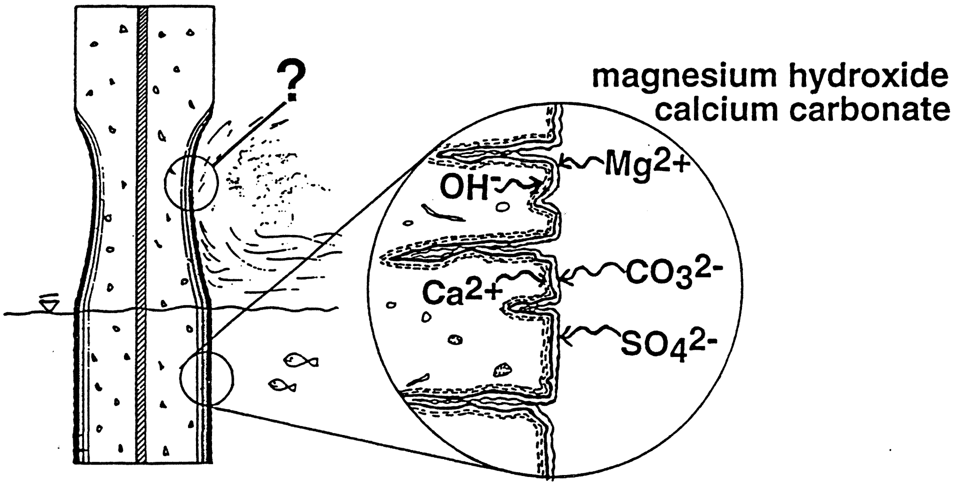


Fig. 39. Magnesium and carbonates from sea water combine with calcium and hydroxides from concrete to form a dense precipitate on the concrete surface and in cracks. This self sealing effect is very pronounced for submerged concrete /39/, but remains to be studied more in detail for concrete exposed to wetting and drying. Similar self sealing effects have been found for deicers containing magnesium (Ca Mg Acetate - CMA) /6/, but less is known on the effect of NaCl and $CaCl_2$ based deicing salts.

The self sealing effect of concrete exposed to sea water is probably at least another major mechanism behind the many observations of marked reductions in the chloride penetration rate, the "effective chloride diffusivity", in concrete over time /31,42/. In Fig. 36, a typical example of a decreasing calculated effective chloride diffusivity over time was shown, as calculated from total chloride profiles at various lengths of submerged field exposure /31/.

The binder type and the binder density of the concrete influence the self sealing process, since the type of the binder will affect the ability of the concrete to release the ions needed for the self sealing precipitation. Very dense concrete with very low solubility will have a strong positive effect due to the very low permeability in such concrete, if the matrix is crack free. On the other hand such dense concrete will possibly have a lower self sealing capacity if cracked. The topic remains however to be studied.

7.4.3 Critical crack sizes

The wide variety of exposure conditions that are imaginable in concrete cracks over time makes it very difficult to find reliable quantitative information on critical crack sizes, as described by the crack width at the concrete surface and the crack depth. Some qualitative information is however available:

With permanent and full immersion of the concrete in water, corrosion becomes completely cathodically controlled, as the oxygen diffusion in water filled pores and cracks is very limited. As reported by Moskvin and Alekseev /21,48/, crack widths up to 0.5 mm are safe under such conditions, as indicated in Fig. 40. A less steep potential gradient in a polarisation experiment indicates an easier anodic dissolution of steel, i.e. less resistance to active corrosion.

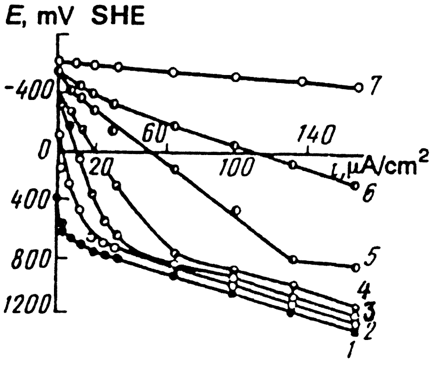


Fig. 40. Curves of reverse anodic polarisation of ordinary steel in concrete submerged in 0.1 M sodium chloride solution. 1- no cracks; 2- crack width 0.1 mm, 3- crack width 0.2 mm, 4- crack width 0.4 mm, 5- crack width 0.6 mm, 6- crack width 1.0 mm, 7- naked steel /21,48/.

Wetting and drying is generally the most aggressive exposure condition for cracked concrete. As illustrated in Fig. 41 by Moskvin /21/, the corrosion rate for cracked concrete is initially high. But the corrosion process slows down over time due to a pore clogging effect of rust in cracks, a phenomenon which does not occur for loose rust on naked steel.

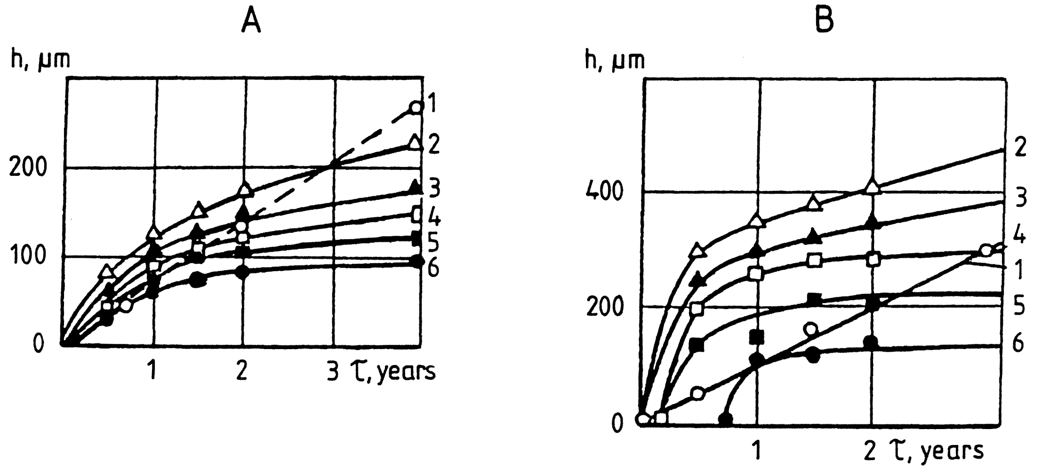


Fig. 41. Corrosion kinetics of reinforcement (depth of pits, h microns) in the crack zone. (A): Atmospheric exposure in Moscow. (B): Cyclic wetting and drying, 1- naked steel, 2- crack width 0.7 mm, 3- crack width 0.4 mm, 4- crack width 0.3 mm, 5- crack width 0.2 mm, 6- crack width 0.1 mm. Note the delayed effect of small crack widths, /21/. h is the depth of corrosion.

No quantitative information exists on when the positive effect of pore clogging by rust will be counteracted by the expansion - cracking effect of accumulated rust. This limit is influenced by the crack width, the geometry, the cover size, the environmental characteristics and the concrete strength. However, the negative effect of a given crack naturally decreases with increasing cover thickness and concrete strength /21/.

The delayed negative effect of small crack widths is probably a result of very slow changes of the local environment close to the crack compared to what is the case for wide cracks.

Long term (10 years) field exposure tests of cracked concrete in urban, industrial and marine coastal atmospheric and tidal zones reported by Schiessl /60/ have indicated the superior long term crack sealing effects of concrete as illustrated in Fig. 42, (A). In Fig. 42 (B), similar findings from more than 10 years of cyclic wetting (100 cycles/year), are presented as originally reported by Verbetskii in /48/.

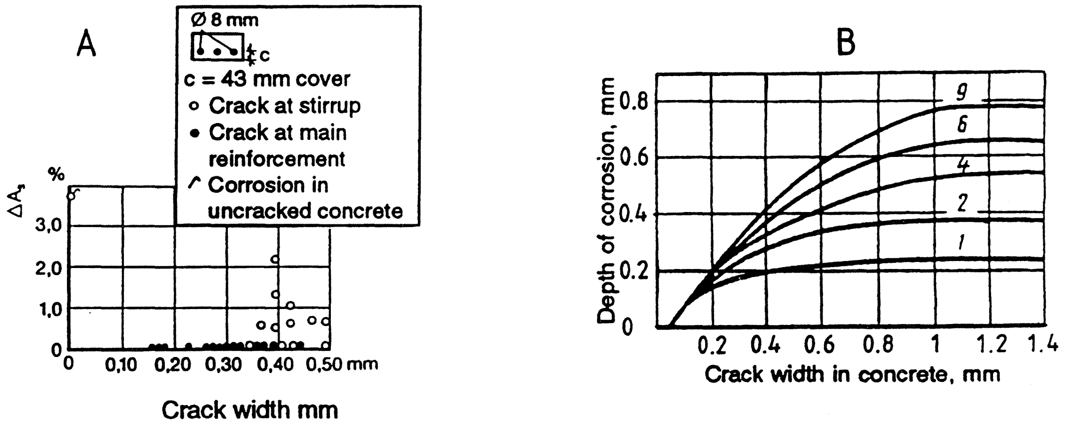


Fig. 42. (A): Corrosion intensity, as measured by the percentage of the reduction in the steel cross section area, for ordinary steel in concrete after 10 years of tidal exposure at the North Sea /60/ (w/b 0.7, 43 mm cover thickness). (B): Corrosion depths for steel reinforcement in concrete after laboratory exposure consisting of 100 wetting-drying cycles/year. The values on the curves denote the number of years /48/ (w/b 0.50).

According to the results by Schiessl, cracks with a maximum width of 0.35 mm would be harmless if the cover is more than 43 mm thick. Verbetskii found that if the crack width is less than 0.2 mm, any initial corrosion ceases after 2 years at a maximum corrosion depth of 0.2 mm. For cracks wider than 1.0 mm, no effect of crack sealing was found on the corrosion rate. Under the exposure conditions set up by Verbetskii, crack widths < 0.4 mm appear to be harmless.

On the other hand, by periodic drying and wetting with a 3% sodium chloride solution, Verbetskii found corrosion depths of 1.5 mm after 2 years of exposure for 0.2 mm crack width, and 3 mm after 7 years of exposure for 0.3 mm crack width /48/. Apparently, periodic exposure for deicing salts of cracked concrete would be more harmful compared to marine exposure, for reasons previously discussed.

However, also for periodic wetting and drying with a 3% sodium chloride solution, Verbetskii found corrosion rates decreasing with time, indicating a crack sealing effect also for concrete exposed to deicing salts.

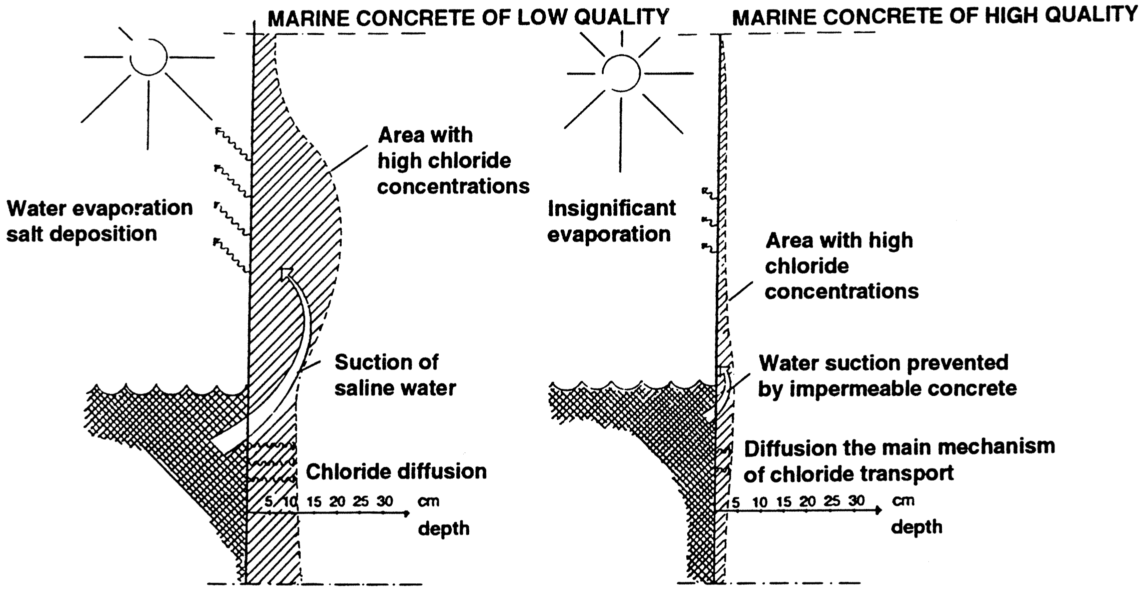


Fig. 43. The effect of low permeability of the concrete on the micro climate affecting the reinforcement. A concrete with a low permeability will develop a constant and passivating environment at the reinforcement, whereas a case with high permeability will have a highly varying inner moisture level /44/.

The effect of decreasing the water to binder ratio of the concrete can be illustrated in quite opposite ways as is shown by Figs. 43 and 44. In Fig. 43, Tuutti illustrated the effect of a more impermeable cover on the micro climate inside the concrete /44/. In Fig. 44, the dense concrete has cracked, due to thermal or plastic shrinkage, giving rise to two speculative scenarios:

Scenario 1. *Crack sealing terminates pitting corrosion.* The geometry of the crack, the accumulation of corrosion products in the crack, and the crack sealing capacity of the binder in a given environment favour the repassivation of any pitting corrosion initiated by water, chloride and oxygen transport in the crack. Open cracks are therefore gradually sealed, terminating the corrosion in the crack.

Scenario 2. *Accelerated pitting corrosion in the crack.* Cyclic salt spraying, wetting and drying of the crack will accumulate chlorides inside the crack. The water suction by the semi-dry concrete favours the water movements and salt deposition within the crack. Thus the free chloride concentration in the crack may become very high. If the anodic pit becomes very acid, the self healing process will not be efficient enough to repassivate the corrosion pit.

Therefore, knowing the nature of the chloride attack being localised to certain exposure zones, it appears much more efficient either to replace ordinary steel with stainless steel in the most aggressive zones, or to prepare for cathodic protection to be introduced when necessary. The complicated nature of cathodic protection of reinforcement in semi-dry concrete, as discussed in Chapter 6, and the costs of maintenance, will most probably favour the specific use of stainless steel in some most aggressive exposure zones.

Several very old but not reinforced concrete structure are still in service, some of them being found in quite aggressive environments. Apparently, an elimination of the corrosion problem of steel reinforcement in concrete by using stainless steel would be the most effective measure besides the normal measures in order to achieve a longer service life for concrete structures. These measures include a properly sized cover, a low water to binder ratio, a sufficient use of air entrainment, and the production of a uniform concrete quality.

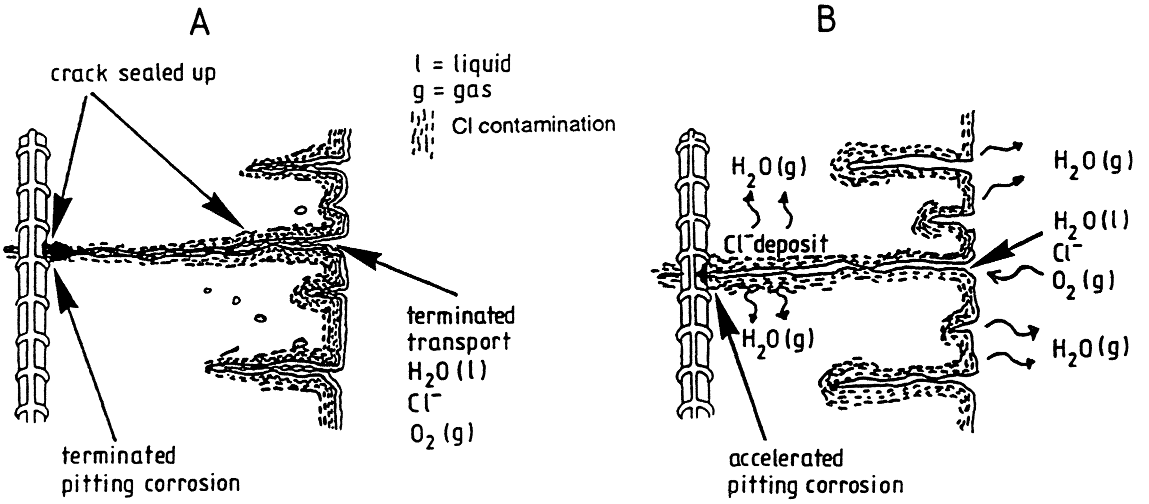


Fig. 44. Two scenarios on the effects of cracks on pitting corrosion in concrete exposed to saline atmosphere. (A): Crack sealing and corrosion products block the transport of water and oxygen and increases the pH-value in the crack, thus inhibiting any pitting corrosion as the crack sealing proceeds. (B). Crack sealing cannot hinder water, chloride and oxygen transport, which are accelerated by salt spraying, wetting and drying, and suction by the semi-dry binder. Chlorides accumulate in the crack, accelerating the pitting corrosion.

Part II - A model for prediction of the corrosion initiation time in reinforced concrete.

8. PREDICTION OF THE INITIATION TIME FOR REINFORCEMENT CORROSION IN CONCRETE

8.1 General

The general parameters controlling the transport of water dissolved ions in concrete are shown in Fig. 45 /61/, derived from Schiessl /62/, Mehta /45/ and Moskvin /21/.

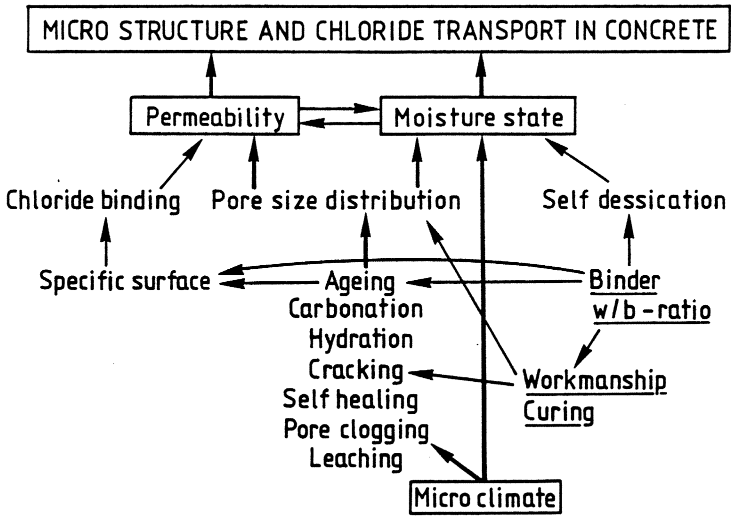


Fig. 45. Various parameters affecting the micro structure and the chloride transport in concrete /61/.

As previously discussed, the initiation time is not associated with a constant critical total chloride concentration in the concrete at the reinforcement. Only "free" chlorides, not being physically or chemically bound by the binder, are interacting with the passive oxide layer protecting the reinforcement from active corrosion.

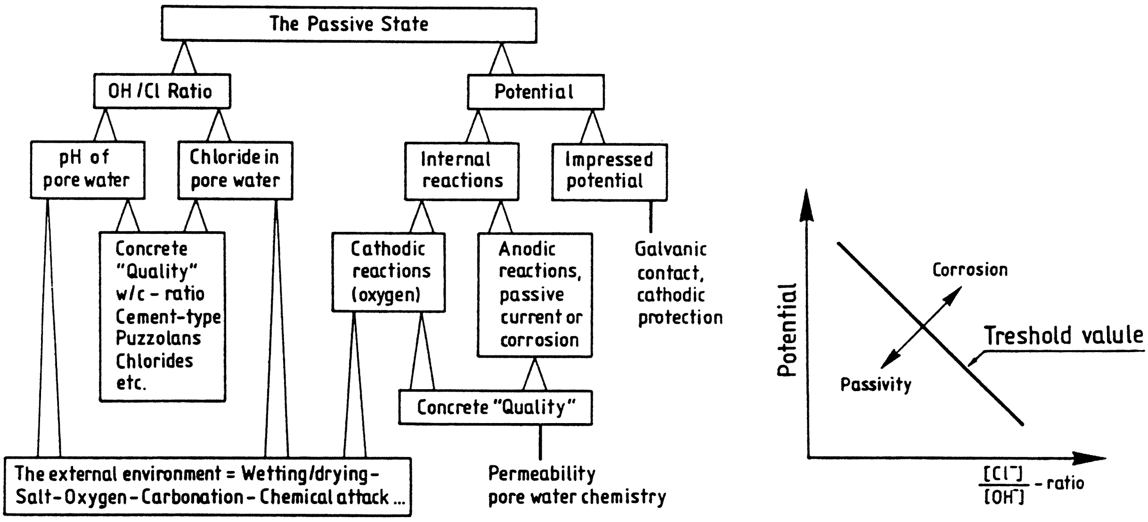


Fig. 46. Various parameters affecting the critical chloride concentration for the initiation of active reinforcement corrosion in concrete /4/.

Furthermore, the critical concentration of free chlorides in the pore solution needed for depassivation of a given steel quality depends on several variables, such as the steel-concrete bonding, the steel potential, the oxygen availability and the alkalinity of the pore solution as indicated in Figs. 14-17. A more detailed presentation of the general parameters controlling the critical chloride concentration for the initiation of active reinforcement corrosion is given in Fig. 46, as presented by Arup /4/.

Water transport determining the moisture state of the concrete has a decisive influence on the chloride transport in concrete in various environments. The moisture state does not only control the transport mechanisms of gases and dissolved ions in the micro structure of a given concrete. By controlling the transport of various aggressive species in concrete, the moisture state also controls the changes in the concrete micro structure over time, such as changes caused by freezing and thawing, alkali silica reactions, sulfate attack, etc.

The moisture state by itself also affects the concrete micro structure in the absence of any transport of external substances into the concrete. Concrete with very low water to binder ratios are known to undergo significant self-desiccation, resulting in binder shrinkage and internal cracking. Internal cracks may, if later interconnected to larger pore systems, facilitate an accelerated transport of moisture and aggressive species into concrete /45/. Typical cracks formed by the self-dessication are however very small, and their effect on the permeability of concrete is uncertain.

The critical crack width and amount of internal cracking in concrete exposed to various environments are not known as discussed previously. As indicated by Schiessl /62/ among others, cracks smaller than 0.35 mm at the surface in most cases do not contribute to gas or ion transport in concrete within a time frame of more than 10 years. The main reasons are probably, (i) self sealing of concrete, (ii) stagnant, non mobile conditions for ions, water and oxygen if cracks are narrow enough. In other words, a system of small cracks apparently acts very similar to the normal pore system in concrete. The self sealing capacity of concrete, if not containing too much pozzolans, makes it less sensitive to cracks compared to most other materials.

The interrelated processes of moisture transport, salt transport, oxygen transport and changes in micro structure, are affected by the local environment. Naturally it is a very difficult task to model such complex phenomena for the large variety of micro climates found at field exposed concrete structures. Nevertheless, computer based simulations of long term effects of interrelated phenomena may be very useful for systematic examinations of a very complex problem. As a complement, detailed field studies of existing structures in various environments may give opportunities to calibrate computer models and models based on detailed laboratory studies.

Furthermore, detailed field studies will give several indications on most important mechanisms and rates of transport and degradation, as well as statistical information. However, generally accepted procedures for sampling and analysis must be agreed upon, before such field data will be useful from a statistical point of view.

8.2 Field chloride profiles as a basis for service life predictions

8.2.1 General

Field studies of existing concrete structures have indicated the complex nature of chloride transport in concrete at various exposure conditions. By evaluating field chloride profiles and thin section micro graphs taken from drilled cores exposed at various locations (various micro climates), it has become evident that the micro structure, the moisture state and the chloride transport rate are all to a large extent affected by the exposure conditions.

As proposed by Poulsen and Maage among others /54,42/, chloride profiles measured on field exposed concrete structures and the chloride diffusivity, measured on drilled cores at standardised exposure conditions in the laboratory, can be used as a basis for the prediction of long term chloride transport rates in concrete.

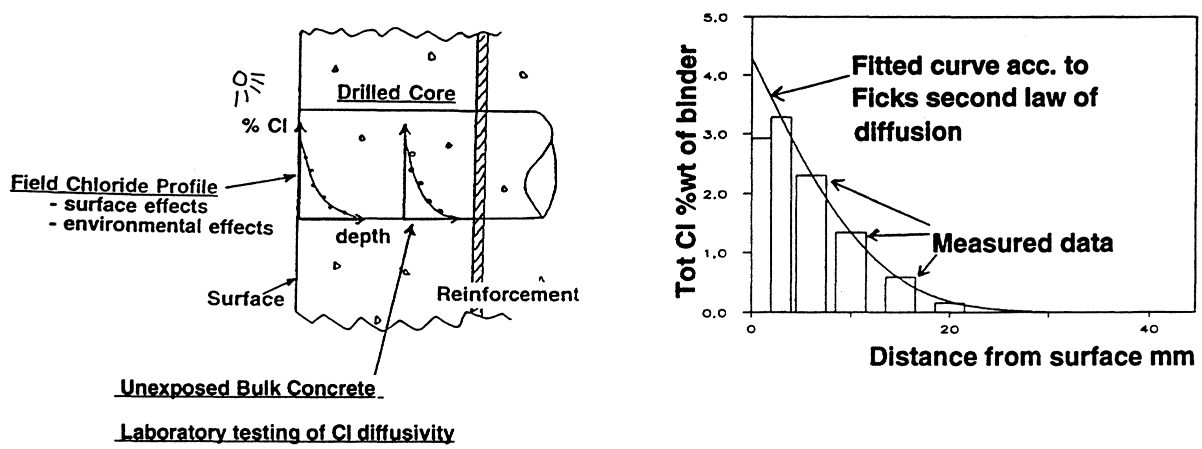


Fig. 47.: Procedure for estimation of the chloride transport rate in concrete, by fitting a measured total chloride profile to Fick´s second law of diffusion. The estimated effective "chloride diffusivity" represents the mean chloride transport rate in the evaluated time period. /31/. The chloride diffusivity measured in the laboratory on unexposed bulk concrete, describes the chloride permeability in a standard exposure condition. /31/.

The chloride transport rate may be evaluated as an effective "chloride diffusivity" by fitting Fick´s second law of diffusion to total chloride profiles measured at various exposure times as indicated in Fig. 47 /31/. Thus, the effective "chloride diffusivity" represents the mean chloride transport rate in the evaluated time period. The calculated "effective chloride diffusivity" over time was illustrated for the submerged part of New Ölandsbron in Fig. 36.

As indicated in Fig. 33, The field chloride profile (as a result of long term field exposure) may vary extensively depending on the micro climate at the sampling position. Therefore, one must select the sampling positions very carefully when field chloride profiles are evaluated after various exposure times, in order to establish relationships for the chloride transport rate over time in various exposure zones.

8.2.2 Models for the long term chloride transport rate in concrete

The following procedure for evaluating long term chloride transport rates in concrete, by using empirical relationships from investigations of field exposed concrete, has been published by Poulsen and Maage et. al. /54, 42/. The procedure is outlined in a flow diagram in Fig. 48:

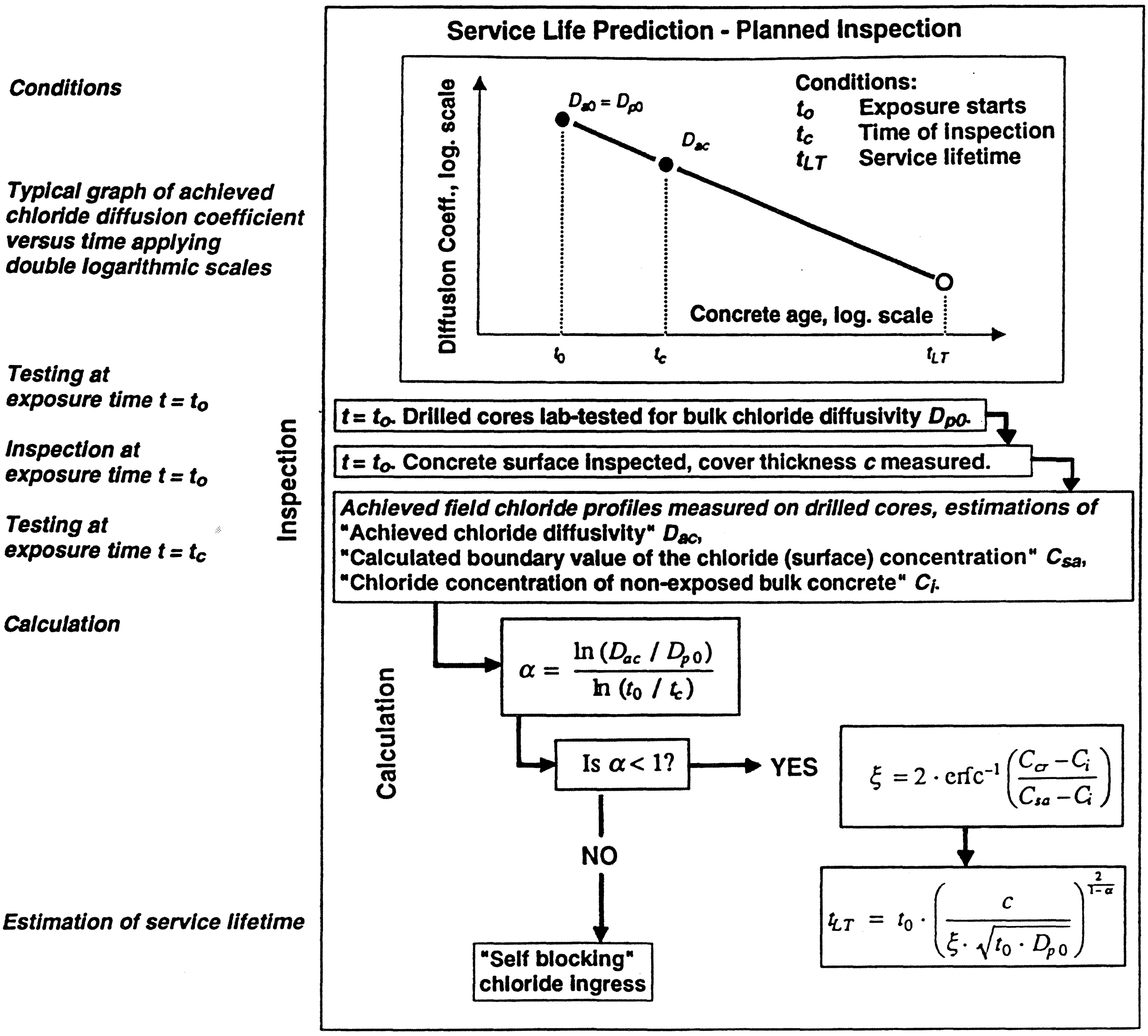
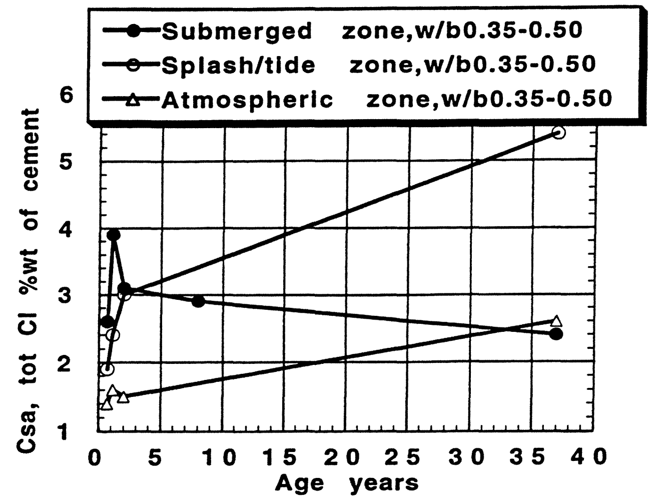


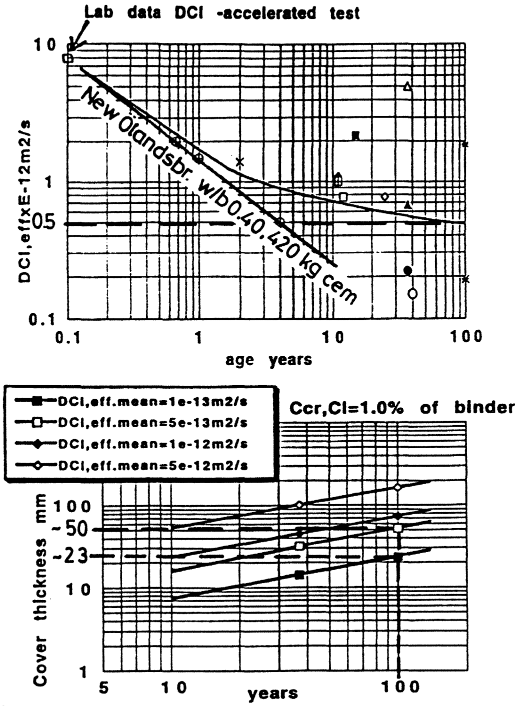
Fig. 48. Flow diagram for the calculation of the corrosion initiation time t_{LT} on the basis of measurements once during the lifetime, as outlined by Poulsen et. al. /54/.

In this model the calculated boundary value of the chloride (surface) concentration, which is used for predicting the future chloride transport rate, does not vary significantly with the age of the concrete. However, as indicated in Fig. 49, the calculated boundary value of the chloride (surface) concentration tends to increase with the exposure time in the tidal- or splash zone. Therefore, the model in Fig. 48 may overestimate the initiation time if a too low calculated boundary value is used for the long term prediction of the chloride transport.

Fig. 49. The calculated boundary value of the chloride (surface) concentration C_{sa} based on field chloride profiles measured on concrete (w/b ratio 0.35-0.5) exposed for 8, 12 and 24 months at the Träslövsläge Field Station, and for 37 years at Esbjerg harbour. The chloride content in the sea water was 14 - 19 g/l.



A simple way to avoid the problem of a varying boundary condition is to use "effective chloride diffusivities" based on field chloride profiles in an iterative procedure; The selected "effective chloride diffusivity" must then correlate to the calculated initiation time as indicated in the flow diagram in Fig. 50:



1) Select an "effective chloride diffusivity" which corresponds to a reasonable initiation time, using field chloride profiles from existing structures exposed in the relevant micro climate for various exposure times.

2) For a given cover size, estimate the initiation time for the selected "effective chloride diffusivity", using extrapolations over time for the "effective chloride diffusivity" selected in (1).

Does the estimated initiation time in (2) differ from the initiation time used in (1)?

Yes ---> Repeat step (1) and (2) using the estimated initiation time.

No ---> The most correct boundary condition has been used when the initiation time used in (1) corresponds to the one used in (2).

Fig. 50 A simple graphical method for an iterative estimation of the long term chloride transport rate in field exposed concrete, based on measured chloride profiles in field exposed concrete at various exposure times.

8.2.3 Field chloride profiles measured in some marine concrete structures

In Fig 51, total chloride profiles at various micro climates for a 37 years old marine concrete exposed in Esbjerg harbour is shown /64/. The concrete was known as being of very high quality, but non-air-entrained. The compressive strength of the concrete was more than 90 MPa, except for in the tidal zone where 70-75 MPa was measured.

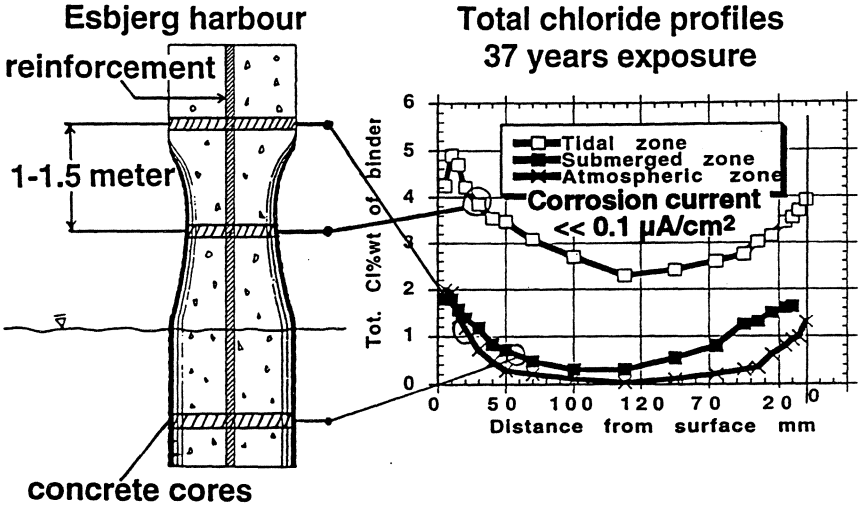


Fig. 51. Total chloride profiles found in a high quality (90 MPa) concrete exposed for 37 years in Esbjerg harbour /64/.

In Fig. 52, calculated "effective chloride diffusivities" based on data from the Norwegian Road Directorate /51/ regarding concrete from several bridges exposed in the marine splash zone has been supplemented by data from, (i) the 37 years old marine concrete in Esbjerg (Fig. 51), (ii) the 4 years old marine New Öland Bridge (Fig. 33) and iii) a 100 years old marine concrete in Japan /67/.

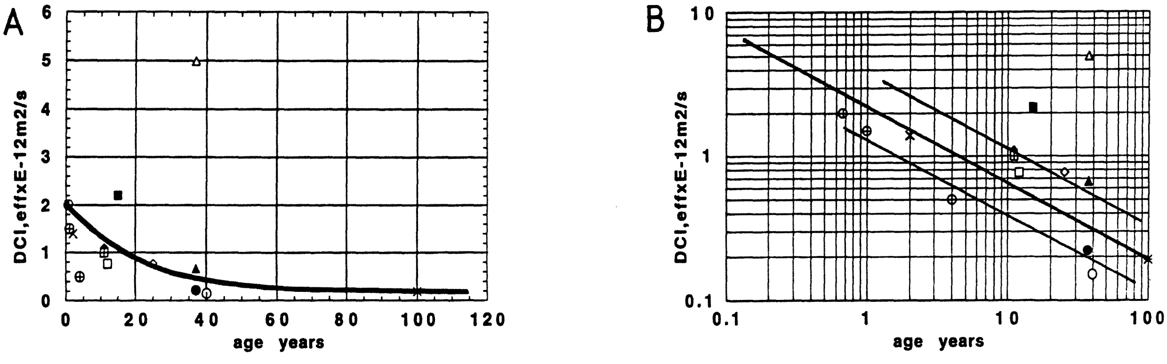


Fig. 52. General information on the chloride transport rate evaluated as an effective "chloride diffusivity" for concrete in the marine splash zone /51,31,67/. In order to compare effective chloride diffusivities from various investigations, the values for $D_{Cl,eff}$ have been recalculated representing mean values from several total chloride profiles from each structure. (A): Linear presentation, (B): Logarithmic presentation.

8.2.4 The effect of micro structural changes on the chloride transport rate over time

Some difficulties associated with the long term extrapolation of chloride transport rates are illustrated in Fig. 53, which is based on the field data in Fig. 52. The very low effective "chloride diffusivity" calculated for a 100 years old marine concrete in Japan /67/ is in contrast to some possible extrapolations of the effective "chloride diffusivity" calculated from concrete with some damage, such as the 37 years old frost damaged concrete in Esbjerg harbour /64/.

To the left in Fig. 53, possible extrapolations are made for degradation phenomena leading to crack propagation, thus increasing the chloride transport rate over time. To the right, a possible scenario on the effect of dead, not propagating, cracks is shown. If the scenarios shown are realistic, it is essential to understand the mechanisms involved in any changes of the degradation rate. Such knowledge will be required in order to critically evaluate the large spread found also for structures with apparently quite similar concrete quality, as indicated in Fig. 52.

More detailed field studies of very old concrete in various climates are necessary in order to improve the accuracy for long term extrapolations of chloride transport in concrete exposed to various environments. However, data should be measured at various exposure times for given details of a concrete structure, in order to obtain information on the changes in the chloride transport rate over time. The usefulness of the data would be much improved if it was stored in common data bases available for statistical treatment.

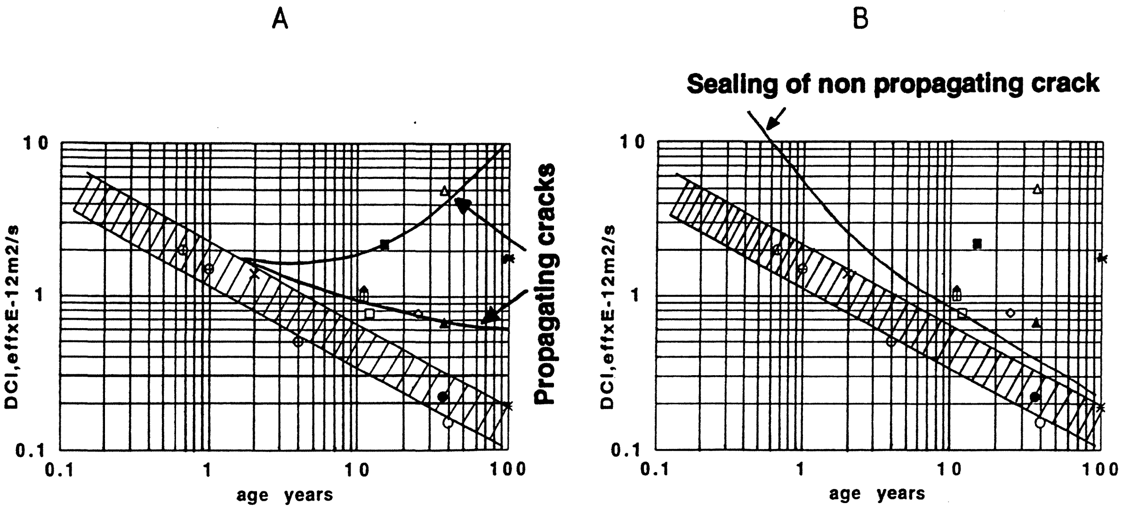


Fig. 53. Scenarios on the effect of various degradation paths on the extrapolation of the effective "chloride diffusivity". The data-points indicated are calculated from measured total chloride profiles in concrete, as shown in Fig. 52. The curves drawn represent various scenarios on the chloride transport rate extrapolated from the data-points. (A): Possible extrapolations for degradation phenomena leading to crack propagation, thus after a certain exposure time increasing the chloride transport rate over time. (B): Possible extrapolation for the case of dead, not propagating, cracks, subjected to crack sealing.

Whenever the time dependency for the chloride transport rate in a given concrete exposed in a given environment is known or can be anticipated, short term field exposure data or standard laboratory data may be used for prediction of the chloride transport rate over time, as illustrated in Fig. 54.

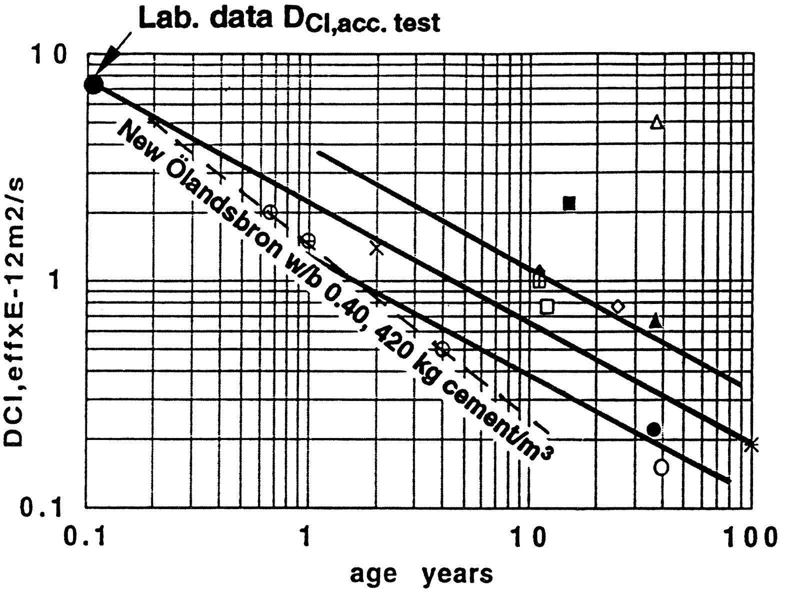


Fig. 54. Short term field exposure data or standard laboratory data for a given concrete may be extrapolated for a given environment, if detailed relationships are known or can be scientifically predicted for the time dependency of such data. The data-points indicated represent field data from Fig. 52. Examples of extrapolations are shown.

8.2.5 Additional information derived from the concrete exposed in Esbjerg harbour

Thin section studies of the concrete from Esbjerg revealed a water to binder ratio of approximately 0.45. No visible damage was found except for a combination of salt scaling and erosion in the tidal zone, resulting in approximately 10 mm loss of concrete cover and another 5-10 mm zone of concrete with no remaining calcium hydroxide in the binder, as indicated in Figs. 55-56.

The remaining concrete cover was 10-30 mm thick, the smallest cover thickness found in the tidal zone. In spite of very careful investigations, only very low reinforcement corrosion rates, < 0.1 μA/cm^2, could be detected /10/.

In addition to the evaluation of total chloride profiles measured in field exposed concrete as summarised in Fig. 52, chloride permeability tests were carried out carefully in a laboratory diffusion cell. This accelerated laboratory testing was carried out using an electrical field according to the methodology developed by Tang and Nilsson /64,84/ on concrete slices from chloride free bulk concrete and on concrete slices from the chloride contaminated surfaces in various exposure zones /64/. Concrete exposed in the atmospheric- and the submerged zone performed in a similar way, with a chloride diffusivity of 4-8 E-12 m^2/s measured in the laboratory test. The chloride free bulk concrete had a chloride diffusivity of 14-16 E-12 m^2/s in the laboratory test, indicating a reduced permeability close to the exposed surface in the atmospheric- and submerged zone.

However, concrete in the tidal zone had a higher chloride diffusivity also 20-50 mm from the surface, 24-28 E-12 m^2/s. The tidal concrete surface was too porous to be tested. The results from the laboratory testing of the chloride permeability are summarised in Table 3.

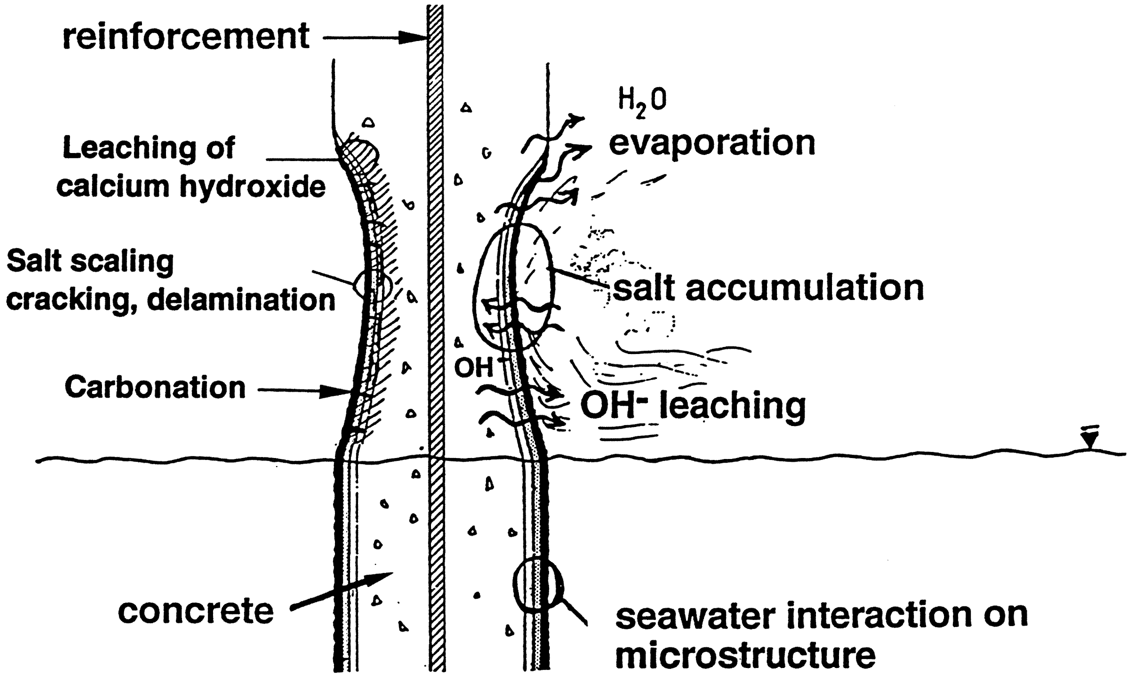


Fig. 55. Some macro- and micro structural changes frequently observed in concrete exposed to a marine environment /21,66/.

Table 3. Chloride diffusivities measured in accelerated laboratory testing of a 37 years old marine exposed concrete /64/.

Exposure zone	Average Chloride diffusivity x E-12 m^2/s
Atmospheric zone	6
Tidal zone, 20-50 mm from surface	26
Submerged zone	7
Unexposed bulk concrete	15

Such field investigations of concrete structures exposed to the nature for a long time appear to be the most valuable test for understanding the concrete degradation mechanisms and degradation rates.

Visible degradation of the concrete was only indicated in the tidal zone, in terms of an eroded surface with the calcium hydroxide being leached to some 10-20 mm depth from the original surface. However, as seen in Fig. 51, the concrete was more or less chloride saturated in the tidal zone.

Salt scaling and ice erosion both proceed as a surface attack on concrete. In most cases the rate of attack decreases with time, depending on to which extent damaged concrete remains as a barrier for future attack. A pessimistic approach, implying that erosion rapidly removes all damaged concrete, results in a linear attack /65/. If a linear attack is assumed, the tidal zone concrete in Esbjerg would suffer from an average surface degradation rate of 20 mm/37 years or 0.54 mm per year.

Thus, if reinforcement corrosion is not considered, a calculated maximum of 54 mm concrete would be lost within a hundred years of exposure. A service life of hundred years would easily be obtained simply by adjusting the thickness of the structure, so that a loss of approximately 50 mm concrete could be accommodated within the designed compressive load bearing capacity. In /65/, a theory is presented on how the synergy between frost attack and corrosion can be treated.

If reinforcement corrosion is considered, the problem may become more serious. The concrete was more or less saturated with chlorides in the tidal zone already after 37 years of exposure, as indicated by the total chloride profile shown in Fig. 51. Also in the atmospheric zone, the chloride level was high.

As indicated in Fig. 56, extensive leaching has brought the alkalinity of the concrete down to the buffer level for calcium hydroxide, pH 12.5. In the tidal zone, pH is even less close to the surface due to extensive removal of calcium hydroxide.

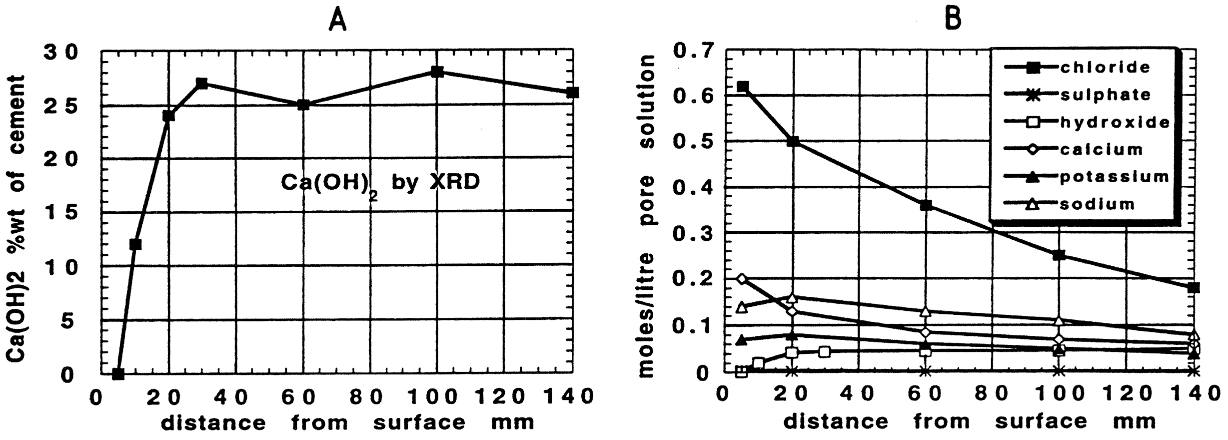


Fig. 56. Analysis of the concrete exposed in the tidal zone of Esbjerg Harbour (A): Calcium hydroxide profile, (B): Soluble ion profile /22/.

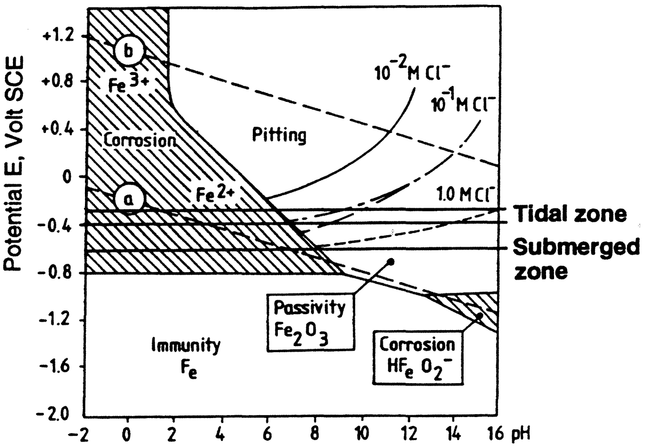


Fig. 57. Passive steel potentials measured in the submerged- and tidal zones, for a 37 years old concrete exposed in Esbjerg Harbour /11/.

In Fig. 57, the passive steel potentials measured in the submerged zone and tidal zone at Esbjerg are shown. As indicated, reinforcement corrosion of any practical danger is impossible in the submerged zone due to the very low potential.

As previously discussed, the only parameter lacking for a corrosion initiation in the tidal zone would be oxygen, provided that an oxygen flow could rise the steel potential into the dangerous area in Fig. 57 in order to initiate pitting corrosion.

Cracks formed in the submerged zone or in the lower tidal zone do not necessarily initiate pitting corrosion, if the steel potential would remain sufficiently low despite the cracking. In other words, the reinforcement would be cathodically protected at potentials where pitting is impossible according to Fig. 14.

On the other hand, the steel potentials are higher and the oxygen more available in the upper tidal and atmospheric zones. A single crack might be enough to initiate pitting corrosion. Whenever initiated, pitting corrosion at such high levels of chloride and moisture would propagate very fast.

The service life of the reinforcement may be lost within a few years after the initiation of pitting corrosion, as illustrated by Fagerlund in Fig. 58.

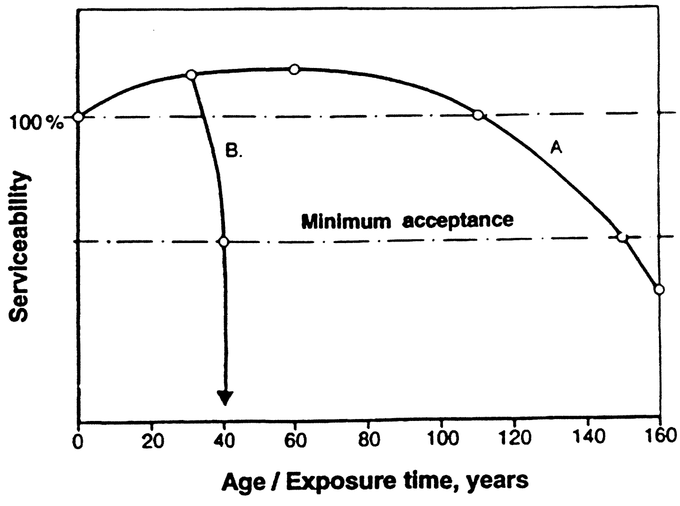


Fig. 58. Principals of the service life of a concrete structure. A) Reinforcement pitting corrosion is not initiated. The degradation rate of the concrete itself is decisive. B) Reinforcement pitting corrosion is initiated in wet, oxygen rich concrete. The degradation rate of the reinforcement is decisive /63/.

9 A MODEL FOR THE CALCULATION OF INITIATION TIME FOR REINFORCEMENT CORROSION IN CONCRETE EXPOSED FOR SALINE ENVIRONMENTS

9.1 General

A model for the initiation time for reinforcement corrosion in concrete exposed to various environments is outlined, taking the effects of micro climate, steel potential, oxygen availability, concrete alkalinity and micro structural changes into account. A general illustration of the model is shown in Fig. 59.

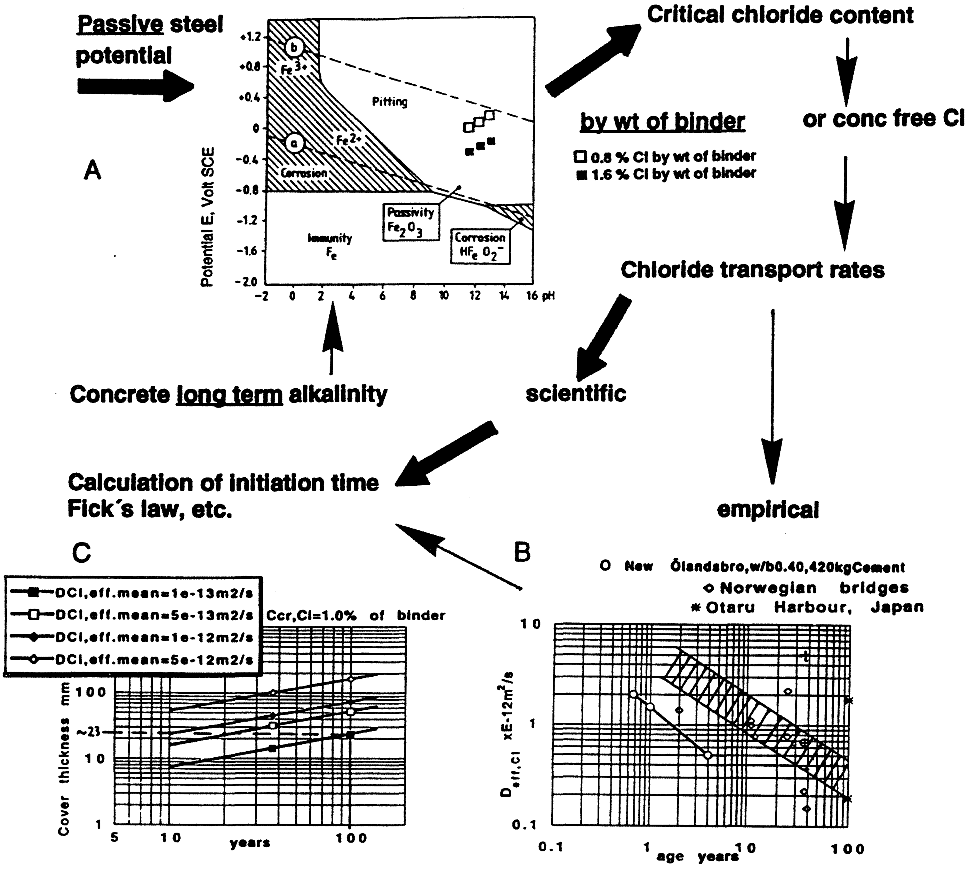


Fig. 59. A model for the calculation of initiation time for reinforcement corrosion in concrete exposed for various saline environments. (A): Estimations of the long term critical chloride concentration based on passive steel potentials and concrete alkalinity at the reinforcement. (B): Estimations of the chloride transport rate in concrete from exposure start until corrosion initiation. (C) Calculation of the initiation time by the use of estimated chloride transport rates and critical chloride concentrations.

Estimations of the long term critical chloride concentration for a given concrete in a given environment should be based on laboratory and/or field data for concrete, by knowledge on the passive steel potentials, on the alkalinity at the reinforcement, on the concrete temperature and the steel-concrete interface properties. The long term alkalinity can be predicted using hydroxide permeability data in a similar way as outlined for the long term chloride transport in concrete. Or, it can be assumed to be pH 12.4, which is an assumption on the safe side for most high quality concrete.

The chloride transport rate can be estimated for a given concrete in a given environment, using mathematical models to relate laboratory measured parameters affecting the chloride transport rate to the corresponding long term behaviour in the field. Such models can be purely empirical or based on scientific knowledge about parameters affecting the chloride transport rate in concrete. The consequences of variations in the micro structure of the concrete, the reinforcement and the environmental characteristics should be treated statistically.

9.2 Examples of calculations of initiation times or of required cover sizes

9.2.1 General

The following environmental exposure zones are considered for concrete structures exposed to marine or deicing chlorides:

a) Submerged zone	marine exposure
b) Tidal zone	marine exposure
c) Tunnel/basin	one side submerged, one side atmosphere
d) Splash zone	deicing salts or marine exposure
e) Atmospheric zone	deicing salts or marine exposure

9.2.2 Estimation of long term steel potential, moisture state and oxygen availability

The steel potential, the moisture state and the oxygen availability in concrete have a decisive influence on the corrosion properties of steel in concrete.

Steel potentials are either measured on the actual structure after several years of exposure in the actual environment, or based on experience from long term observations on other structures in the relevant environment, as listed in Table 4.

The following must be noted: (i) The steel potentials may fall over time as oxygen gradients grow steeper. This is frequently observed for water saturated concrete. (ii) Measurements of steel potentials in semi-dry concrete using external reference electrodes often results in measurement errors in the range of 100-200 mV.

The hygroscopic nature of chlorides will for most outdoor concrete structures ensure the presence of electrolyte for the development of pitting corrosion on steel in the concrete. However, for very wet concrete, water saturated pores will significantly restrict the oxygen availability for the corrosion process. Moisture and oxygen will in turn affect the steel potential.

In Table 4, expected values are given for the long term steel potentials, the moisture state, the oxygen availability and the corrosion risk in various exposure zones, as outlined in the previous chapters.

Table 4. Expected values for long term passive steel potentials, moisture state and oxygen availability in concrete.

Exposure zone	Passive steel potential relative to SCE	Moisture state at rebar, > 30 mm cover	Oxygen availability at rebar	corrosion risk
Marine, submerged zone	< - 600 mV	saturated when Cl reaches the rebar	insignificant	insignificant corrosion rate if initiated
Marine, tidal zone	-200 to -700mV varies with oxygen, cover, age, concrete quality	saturated if not seriously cracked	high only if seriously cracked	low except for in oxygen rich areas, large cracks voids etc.
Submerged tunnel/basin exposed to the atmosphere on one side	+150 to -700 mV, extensive drying, steep gradients	varies with the concrete quality and geometry	varies with the concrete quality and geometry	high if the steel is affected by steep gradients
Splash zone (marine, or deicing salts)	+150 to-200mV varies with oxygen, cover, age, concrete quality	semi-dry, varies with cover size, concrete quality	high	high if Cl accumulates in cracks and when Cl reaches steel
Atmospheric zone (marine, or deicing salts)	+150 to-200mV varies with oxygen, cover, age, concrete quality	semi-dry, varies with cover size, concrete quality	high	high if Cl accumulates in cracks and when Cl reaches steel

Note the high tolerance for chlorides in water saturated concrete with low availability of oxygen. Active corrosion of practical significance will only be initiated under the following conditions: The availability of oxygen is high enough to (i) depolarise the steel to a potential above the critical pitting potential, ii) maintain the cathodic oxygen reduction at a significant rate.

Active corrosion initiated below the critical pitting potential proceeds at a rate which is in most cases practically insignificant, provided that the reinforcement is properly embedded in concrete.

9.2.3 Estimation of long term alkalinity at the reinforcement

The alkalinity of concrete pore solution in contact with steel affects the critical chloride concentration for initiation of active reinforcement corrosion.

The long term alkalinity of the pore solution is either predicted using empirical observations of long term exposed concrete in the field. Or the hydroxide permeability can be predicted using data for chloride permeability as described by Sergi et. al. in /75/. A schematic illustration is given in Fig. 60 as presented by Andrade et. al. in /127/.

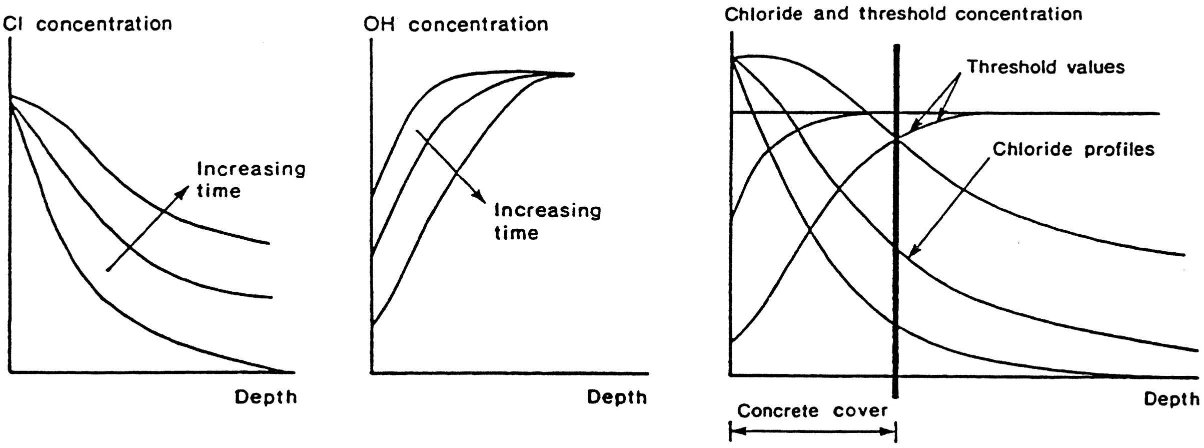


Fig. 60. Schematic illustration of the changes over time in chloride concentration, alkalinity and critical chloride concentration at the reinforcement for a given concrete quality, cover size and set of exposure conditions /127/

The following should be noted: (i) The alkalinity of the pore solution in concrete varies significantly over time due to carbonation, leaching etc. Alkali hydroxides are highly soluble and thus strongly affecting the alkalinity as expressed by the pH value. Hydroxides are more mobile in concrete as compared to chlorides. In normal concrete, the amount of alkali hydroxide produced is only about 5-10% of the amount of the less soluble calcium hydroxide produced. Thus, as hydroxides are leaving field exposed concrete, the pH-value approaches the buffer level of calcium hydroxide, approximately pH 12.4-12.5.

(ii) Pozzolans in concrete reduce the amount both of alkali hydroxides and of calcium hydroxide formed in the concrete. Removal of alkali hydroxide is on the other hand regarded as positive with respect to expansive alkali silica reactions, and some other destructive mechanisms. However, extensive addition of pozzolans may provide insufficient amounts of calcium hydroxide for the long term prevention of pitting corrosion /120/.

(iii) No accurate method exists today for measurements of the pore solution composition of dense, high quality concrete.

9.2.4 Estimation of the critical chloride concentrations at the reinforcement

Various exposure zones correspond to various passive steel potentials and pH-values for the pore solution of concrete as discussed in 9.2.2 and 9.2.3. In Fig. 15 (B), critical chloride concentrations may be estimated for given values of the steel potential and the pH-value.

Note that the critical chloride concentrations given for reinforced concrete in Fig. 15 (B) are generally higher as compared to the indicated critical concentration lines which are derived from naked steel exposed to saline solutions. Several indications exist, suggesting a higher chloride tolerance for steel in concrete during long term exposure /10,20,120/, for the reasons discussed in Chapters 3-4. Thus, the critical chloride concentrations estimated from the critical chloride concentration lines in Fig. 15 (B) represent a conservative approach resulting in an underestimation of the initiation time for reinforcement corrosion. Future research is necessary to develop reliable potential - pH diagrams for steel in concrete.

9.2.5 Estimation of critical total chloride content at the reinforcement

As discussed in chapter 5, a critical concentration of free chlorides in the pore solution at the reinforcement can be recalculated to a corresponding critical chloride content, expressed as percent of total chloride by weight of binder. Since the pore solution expression method is not usable on high quality concrete, the relationship between free chlorides and total chlorides must be either extrapolated from field exposed concrete of lower quality, or it can be estimated from similar relationships obtained in the laboratory.

A maybe less accurate but certainly more practical procedure would be to establish a data bank of critical chloride contents expressed as percent of total chloride by weight of binder (*measured* on the same sample) and the corresponding passive steel potentials. In addition, the concrete microstructure and the alkalinity at the reinforcement should be documented. This data could then be presented in potential - pH diagrams for concrete of various cover sizes, w/b ratios, cement types, exposure conditions, etc., as illustrated schematically in Fig. 61.

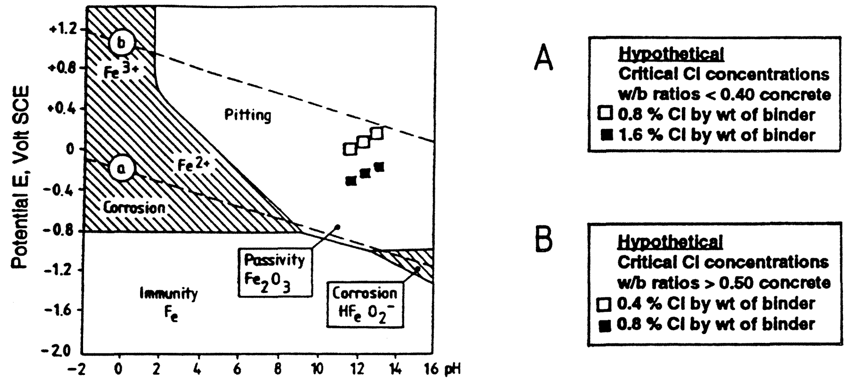


Fig. 61. Hypothetical critical chloride contents in concrete. (A) Concrete of low w/b ratio. (B) Concrete of high w/b ratio.

9.2.6 Estimation of the long term chloride transport rate in concrete

The initiation time for active corrosion may be calculated if the chloride transport rate over time, and the critical chloride concentration for corrosion initiation, are known at various exposure times for the actual concrete in the relevant environment.

Ideally, the required information would be derived from a scientific model taking all relevant factors affecting the chloride transport rate, such as hydroxide leaching, non linear binding, surface densification, moisture transport, cyclic wetting and drying, cracking, etc., into account. In addition, the scientific model should be accompanied by accurate long term field exposure data, including chloride and moisture profiles, etc., from relevant concrete structures exposed for various times in relevant micro environments.

As previously discussed, such scientific models are under development, /55,105/ among others, but still more work is necessary to prove their validity for concrete exposed during long time to the relevant environment.

While waiting for scientific models that are able to predict long term chloride transport into concrete exposed to the real environment such as the very complex splash zone, empirical relationships from field data may be used. However, the scatter in such field data is naturally very high as influenced by the position of the sampling, the sampling procedure, the micro environment, the concrete quality, local defects in the concrete, etc.

An empirical procedure for evaluating long term chloride transport rates in concrete, by using chloride profiles from investigations of field exposed concrete, was discussed in Chapter 8 as derived from Poulsen and Maage et. al. /54,42/, see Figs. 48, 50 and 52.

9.2.7 Estimation of the initiation time for active reinforcement corrosion

The initiation time for a given concrete in a given environment can be calculated for a given critical chloride content, and a given relationship between the effective "chloride diffusivity" and the time, using Fick´s second law of diffusion /54/.

Such calculations are illustrated in Fig. 62 (A), for a Portland cement concrete of w/b 0.45 with a 40 mm cover, exposed in the marine tidal zone. The long term steel potential is supposed to be a maximum of -200 mV (SCE), and the critical chloride content is supposed to be a minimum of 0.4% by weight of cement. 4 different values for the long term prediction of the "effective chloride diffusivity" are used from Fig. 52. As indicated in Fig. 62 (A), an initiation time of 60 years would be calculated for an "effective chloride diffusivity" of 0.2 E-12 m^2/s at 60 years of exposure.

As discussed in Chapters 3-4, the critical chloride content for a high quality concrete exposed in the tidal zone is probably much higher than 0.4% by weight of cement. Therefore, the calculations were repeated using a substantially higher critical chloride content of 1.0% by weight of cement, a value which has frequently been measured for such high quality concrete /14,20,74/. The results from the calculations are illustrated to the right in Fig. 62. As indicated in Fig. 62 (B), an initiation time of more than 150 years would be calculated for an "effective chloride diffusivity" of 0.2 E-12 m2/s at 150 years of exposure.

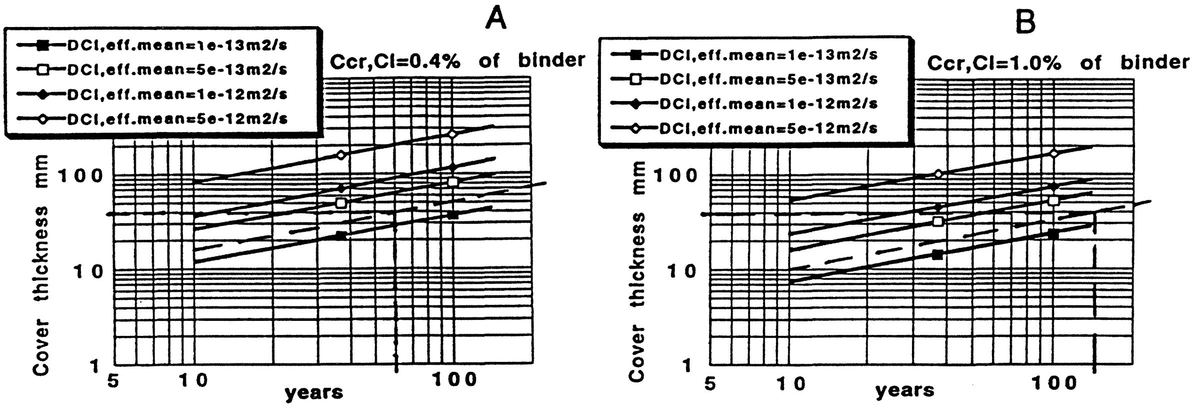


Fig. 62. Examples of calculated initiation times for a given Portland cement concrete of w/b 0.45 and a 40 mm cover, exposed in a marine tidal zone. The passive steel potential used is -200 mV (SCE). (A) A critical chloride content of 0.4% is used. (B) A critical chloride content of 1.0% is used.

As indicated in Fig. 62, a very low long term mean effective chloride diffusivity would result in initiation times in the range of 70 to 150 years for a 40 mm cover, for critical chloride contents ranging from 0.4 to 1.0% by weight of cement. The latter value is likely to be valid for a high quality concrete /14,20,74/.

However, as illustrated in Fig. 52, a much higher long term mean effective chloride diffusivity is not unrealistic, especially not for concrete exposed in the tidal zone. If the line for a mean effective chloride diffusivity of 1.0E-12 m2/s is used in Fig. 62, much shorter initiation times in the range of 12 to 28 years would be calculated, for critical chloride contents ranging from 0.4 to 1.0% by weight of cement. On the other hand, the active corrosion rate may still be extremely low due to the lack of oxygen at the reinforcement. Provided that the steel potential is low enough to avoid pitting corrosion, and that the reinforcement is properly embedded in concrete, such short initiation times will probably not become a serious problem in practise.

In Fig. 63, the effect of using welded austenite type stainless steel (18% chromium, 8% nickel) is calculated for the same splash zone concrete as in Fig. 62, i.e. w/b 0.45, and a 40 mm cover. The steel potential is assumed to be a maximum of -200 mV (SCE). As reported by Sørensen /17/, the critical chloride content measured by weight of binder would increase with at least a factor 4 for this welded stainless steel.

Thus, a critical chloride content 4 x 0.4 = 1.6 % by weight of cement is used to in Fig. 63 (A). In Fig. 63 (B), the same calculation is performed using a slightly higher and more realistic critical chloride content, 2.0 % by weight of cement. The long term predictions of the "effective chloride diffusivity" are similar as these used in Fig. 62.

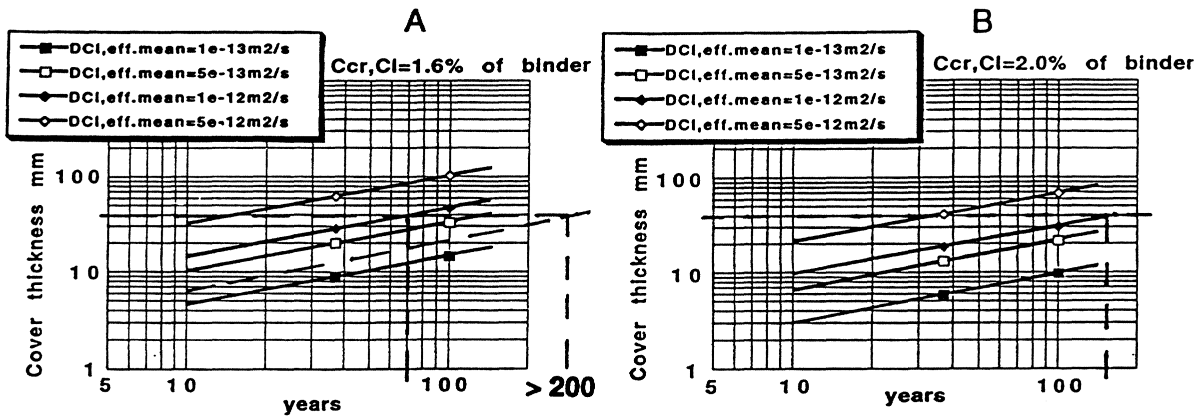


Fig. 63. Examples of calculated initiation times for a given Portland cement concrete of w/b 0.45 and a 40 mm cover, exposed in a marine tidal zone. Stainless steel reinforcement is used in the outer part of the concrete. The passive steel potential used is -200 mV (SCE). (A) A critical chloride content of 1.6 % is used. (B) A critical chloride content of 2.0% is used.

As indicated in Fig. 63, the use of stainless steel would have a dramatic effect on the service life of the concrete considered. An initiation time of more than 200 years is obtained using a mean effective chloride diffusivity of 2E-13 m^2/s. A higher mean effective chloride diffusivity of 1E-12 m^2/s, "damaged concrete", results in initiation times of 75-150 years, depending on the critical chloride content for the stainless steel. It is possible that reinforcement corrosion would no longer restrict the service life of this structure if stainless steel reinforcement is used.

9.2.8 Selection of concrete and reinforcement quality for a given initiation time

Five simplified examples are given on the possible use of the outlined model for materials selection of reinforced concrete. A desired service life of 100 years is used.

A) Concrete in the plash zone and the tidal zone . A good quality concrete is required for long term resistance to salt scaling, erosion, alkali silica reaction, etc. Propagating cracks are probably the rate determining factor for general loss of durability and corrosion initiation. Thus the concrete should have, (i) a high capacity to resist crack formation, (ii) a high crack sealing capacity.

As seen in Table 4 and in Figs. 14-15, oxygen availability will control the critical chloride content for corrosion initiation. The upper tidal and splash zone will be critical, since the tidal zone is most rapidly chloride saturated and the splash zone concrete is rich oxygen. Rapid corrosion as illustrated in Fig. 64 would easily be initiated.

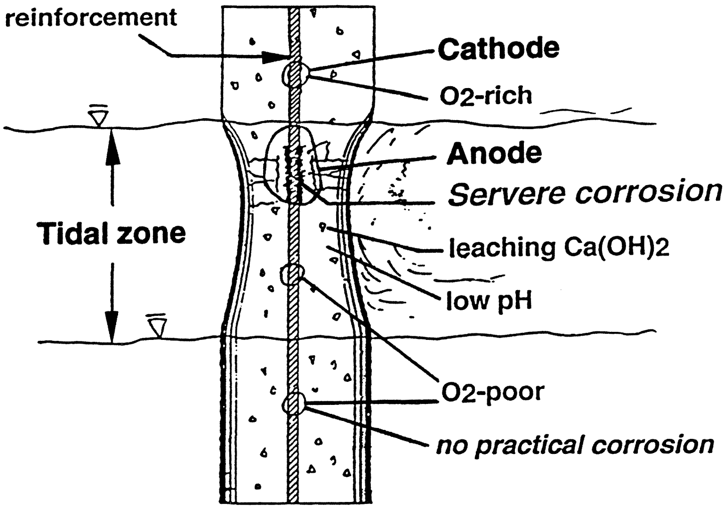


Fig 64. The development of a high intensity corrosion macrocell in the upper tidal zone or in the splash zone of the concrete structure. This accelerated type of corrosion is similar to galvanic corrosion, which sometimes occurs if one metal is corroding in metallic contact with a dissimilar metal, due to differences in electrochemical potential. In the present case the "dissimilar" metals are represented by steel at a high potential in the splash zone being rich in oxygen, and steel at a low potential in the tidal zone with a low oxygen concentration at the reinforcement.

The initiation time is calculated using a high chloride transport rate associated with concrete exposed in the tidal zone, and a low critical chloride content associated with concrete exposed in the splash zone. Long term mean effective chloride diffusivities 0.5E-12 m^2/s ("crack free" high performance concrete) and 5.0E-12 m^2/s (normal concrete) are chosen from Fig. 52. Critical chloride contents of 0.4% by weight of cement for ordinary steel, or 1.6 % by weight of cement for austenitic stainless steel with 18% chromium, 8% nickel, are assumed. The results are shown in Fig. 65.

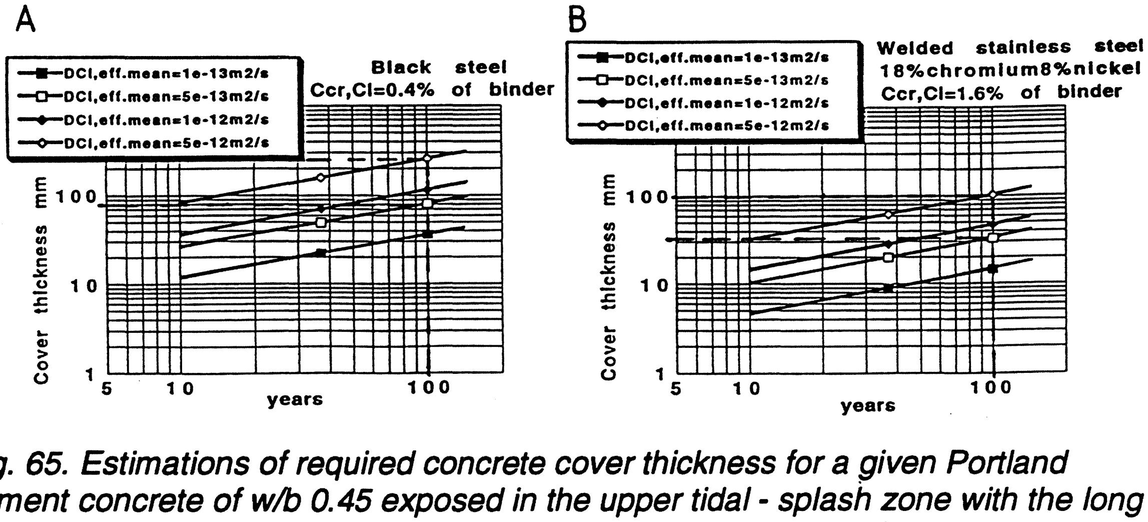


Fig. 65. Estimations of required concrete cover thickness for a given Portland cement concrete of w/b 0.45 exposed in the upper tidal - splash zone with the long term effective chloride diffusivities 0.5 E-12 m^2/s and 5.0E-12 m^2/s. (A): Ordinary steel, critical chloride content 0.4% by weight of cement. (B): Stainless steel, critical chloride content 1.6% by weight of cement.

The required concrete cover is estimated by Fig. 63, to be in the range of 80 to 250 mm for ordinary steel and 32 to 100 mm for stainless steel, for long term mean effective chloride diffusivities ranging from 0.5E-12 m^2/s to 5.0E-12 m^2/s.

If ordinary steel and high performance concrete are chosen in order to achieve an initiation time of 100 years, considerations should also be taken for (i) crack prevention, (ii) preparation for cathodic protection.

If stainless steel is chosen, considerations should also be taken for (i) the quality of the stainless steel, the welding technique, mechanical properties etc., (ii) the effect of chloride accumulation if propagating cracks are admitted.

A combination of high performance concrete and stainless steel seems to be the most suitable choice.

B) *Concrete exposed for deicing salts in the splash zone.* Similar to A), a very good general durability towards frost, chemical attack, etc. is required. This concrete is rich in oxygen, thus a critical chloride content 0.4 % by weight of cement is used. Long term mean effective chloride diffusivities taken from Fig. 52 cannot be used without confirmation, since the pore blocking effect of normal deicing salts is not as efficient as the pore blocking effect associated with sea water. Thus, the long term mean effective chloride diffusivities 0.5E-12 m^2/s and 5.0E-12 m^2/s are chosen with precaution.

The required concrete cover is estimated by Fig. 63, to be in the range of 80 to 250 mm for ordinary steel and 32 to 100 mm for stainless steel, for long term mean effective chloride diffusivities ranging from 0.5E-12 m^2/s to 5.0E-12 m^2/s. The same considerations as in A) applies also for the use of high performance concrete and/or stainless steel for concrete structures exposed to deicing salts in the splash zone.

Similar to A), the required concrete cover is estimated in Fig. 63, for ordinary steel (left) 250 and 80 mm, and for stainless steel (right) 100 and 32 mm, for long term mean effective chloride diffusivities 5.0E-12 m^2/s and 0.5E-12 m^2/s respectively.

C) *Submerged tunnel/basin exposed to the atmosphere on one side and to chloride containing water on the other side.* Cracking and oxygen availability will control the initiation time. Any development of gradients will facilitate the development of a high intensity corrosion cell similar to that shown in Fig. 64, provided that oxygen is frequently available. Any salt accumulation will accelerate the concrete degradation and the reinforcement corrosion.

Initiation times are unpredictable since critical chloride contents and chloride transport rates may vary with orders of magnitude. Most probably the reinforcement will face steep gradients in moisture, oxygen and chloride.

Ordinary steel would only be safe if placed in (i) continuously water saturated concrete, (ii) semi-dry, not carbonated concrete, far away from the evaporation front where salts are deposited, (iii) very dry concrete subjected to carbonation but no salt exposure, see Fig. 66.

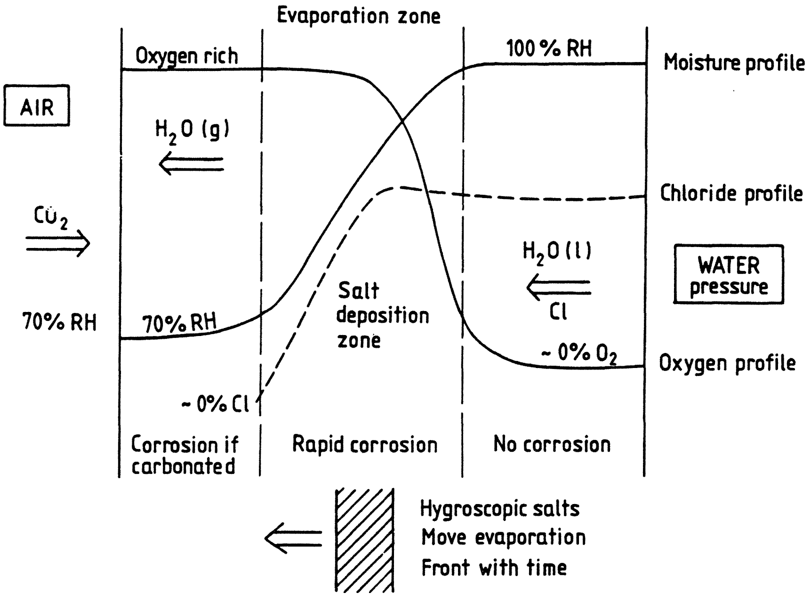


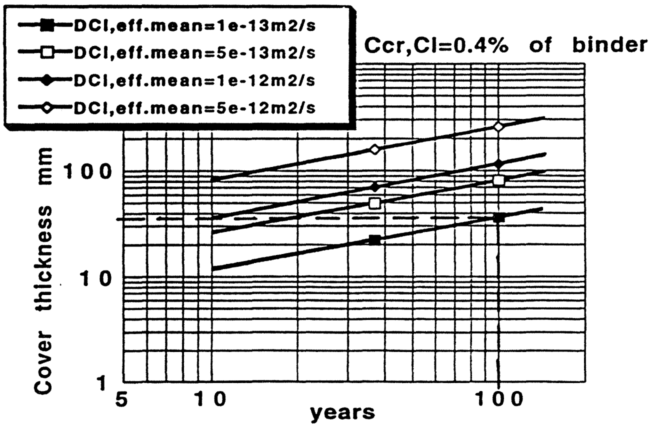
Fig. 66. Illustration of areas sensitive to corrosion in a submerged concrete wall subjected to drying from one side and exposed to saline water on the other side .

The same considerations as in A) applies also for the use of high performance concrete and/or stainless steel in a submerged tunnel/basin exposed to the atmosphere on one side.

D) *Submerged concrete.* A good quality concrete is required for long term resistance of the binder to sea water attack. Looking at Table 4 and Fig. 57, an expected passive steel potential of less than -500 mV indicates a critical chloride concentration in the order of 1.0M, i.e. > 35.5 g/l. Normal sea water has a maximum chloride concentration of approximately 19 g/l. Thus, corrosion is not likely to determine the service life of the concrete. Ordinary steel may be used.

E) *Concrete exposed to the atmosphere* (above the splash zone). A concrete of reasonable high quality is required for long term durability. A critical chloride content of 0.4 % by weight of cement is used for uncarbonated concrete being rich in oxygen. Since the chloride load in the atmospheric zone is considerably less than in the splash zone, a maximum long term effective chloride diffusivity of 1E-13 m^2/s will be on the safe side. The required concrete cover thickness is estimated to be 35 mm in Fig. 67.

Fig. 67. Estimation of the required concrete cover thickness for concrete exposed to atmospheric conditions with the long term effective chloride diffusivity 1.0E-13 m^2/s. For ordinary steel the critical chloride content is supposed to be 0.4% by weight of cement.



9.2.9 Effect of cracks on the initiation time for active reinforcement corrosion

The effect of cracks on the initiation time for active corrosion of steel in concrete may be predicted using 3 scenarios. Cracks are divided into (i) "dead" cracks with a constant micro environment inside the crack, thus the cracks are not propagating with increased time, (ii) "dynamic" cracks with a changing micro environment inside, thus the cracks are growing over time.

Scenario A) *Cracks in submerged concrete not resulting in significant oxygen transport to the reinforcement.* Such cracks are probably harmless as long as they do not propagate with time. As long as oxygen is practically not available for the cathodic reaction to proceed, chloride initiated reinforcement corrosion is not likely to control the service life of submerged concrete.

Scenario B) *"Dead" cracks penetrated by chlorides in concrete exposed to the air.* The main effect of non propagating cracks would be a reduced effective cover thickness. As a first approximation, the initiation time may be predicted by subtracting the nominal cover thickness with the measured mean crack depth, as indicated in Fig. 68. The reduced effective cover thickness and an estimated long term effective chloride diffusivity for uncracked concrete would then be used for the initiation time prediction.

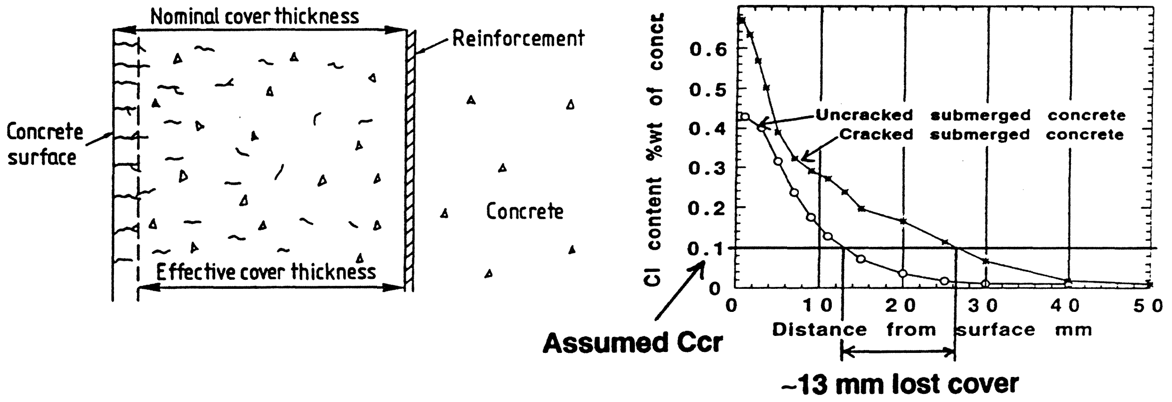


Fig. 68. Procedure for calculation of the effective cover thickness for a concrete with a large number of small, "dead" cracks. If experimentally obtained chloride profiles exist from cracked and uncracked concrete exposed in a similar environment, the "lost cover" may be calculated from the difference in chloride penetration depth for the anticipated critical chloride content for corrosion initiation.

Scenario C) *Dynamic cracks that are large enough to facilitate a changing micro environment inside the crack.* Such cracks are unstable over time and will propagate in an unpredictable manner. The corrosion initiation time cannot be predicted without proper predictions of the crack propagation, requiring detailed knowledge of the fracture mechanics of such cracks over time. However, the initiation time is likely to be short compared to concrete with only small, dead cracks.

The classification of various cracks in various concrete qualities exposed to various environments require detailed long term field studies. The critical crack size, as described by width, depth, geometry, will probably vary with the concrete quality, the design, the cover thickness and the micro climate as discussed in Chapter 7.

10. CONCLUSIONS, RECOMMENDATIONS AND RESEARCH NEEDS

10.1 General

In this chapter some conclusions are drawn from the previous chapters. Some suggestions on the choice of concrete materials and on research needs are given.

10.2 Choice of concrete materials

An optimal choice of concrete materials and quality will naturally vary with the exposure conditions, the type of structure and the desired service life. However, the cover thickness in a reinforced concrete structure will have a decisive influence on the service life, since the cover concrete acts as a physical protection for the rest of the concrete structure. Besides a general recommendation of a thick enough concrete cover, the following remarks are given on the choice of concrete materials:

In hot climates such as in the Middle East, high temperatures, extensive drying, cycling of temperature and wetting and drying are known to favour rapid salt accumulation in concrete, causing cracking and rapid reinforcement corrosion /21,25/.

In cold climates with several events of freezing and thawing, such as in Scandinavia and at the coastline of Canada and Russia, or in concrete that is frequently exposed to deicing salts, saline freezing and thawing is considered as causing the most rapid degradation of concrete /21/.

The optimal choice of concrete from an economical and technical point of views, depends on the desired service life and the exposure conditions.

In marine exposure, associated with several cyclic degradation mechanisms such as freezing and thawing, wetting and drying, cyclic temperatures etc., very dense concrete qualities are probably less favourable since they are more brittle and therefore more prone to crack. Furthermore, such a concrete probably has less self sealing capacity /39/. Thus, a very dense and very brittle concrete probably also have less crack sealing capacity compared to a concrete with a distinct buffer of calcium hydroxide.

Note that under such severe exposure conditions the degradation is generally believed to be triggered by crack formation, making the transport channels open for moving water to accelerate the deterioration rate /21,25,33/. Therefore it is the long term permeability of the cracked concrete rather than that of the uncracked concrete which becomes likely to control the rate of degradation.

However, under more static exposure conditions or when high strength rather than a long service life is desired, then the denser and stronger concrete appears optimal. Examples in this category, with relatively short desired service life, 20-40 years, would be industry floors and concrete roads.

Field exposure of high strength concrete in Norway, north America and elsewhere have indicated exposure times more than 20 years before any salt scaling attack would develop to any significance.

10.3 Selective use of stainless steel in concrete

10.3.1 General

Regardless of climate type, the attack is usually concentrated to some most exposed zones, such as at an evaporation front, at edges subjected to extreme temperature and moisture cycles, at salt spray zones, etc., as illustrated in Fig. 28. These exposure conditions will all favour cracking of the concrete and transport of moisture, salts and oxygen into the concrete. In other words, such conditions will favour a rapid development and propagation of pitting corrosion on ordinary steel in concrete.

Once initiated, the active pitting corrosion will become the most rapid degradation mechanism limiting the service life of the structure. Pitting corrosion rates of 5-10 mm/year have been reported for some extreme field cases /16/, indicating that the remaining service life of the reinforcement may be lost within a few years after the initiation of the pitting corrosion.

On the other hand, the degradation rates for freezing and thawing, salt crystallization, etc. on good quality concrete (water to binder ratios < 0.50) is considerably slower compared to pitting corrosion in concrete exposed to the atmosphere. Several field studies of very old concrete mixes have indicated the comparably slow degradation rate for concrete mixes of low water to binder ratios as long as reinforcement corrosion is not initiated /21,25,41,43/.

Furthermore, the effects of surface scaling and cracking are much less pronounced on the concrete compressive strength compared to the negative effect on the tensile strength caused by pitting corrosion of the reinforcement.

Thus, it may be concluded that a long service life (>100 years) of concrete structures may quite easily be achieved by using a low water to binder ratio as the principal measure besides the use of a large enough cover, as long as active pitting corrosion of the reinforcement is not initiated.

The traditional measures aim at delaying the corrosion attack, by increasing the initiation time for pitting corrosion in concrete in a given environment. Traditionally, the corrosion initiation is delayed by either (i) increasing the cover thickness,
(ii) decreasing the water to binder ratio, thus decreasing the uncracked permeability,
(iii) increasing the amount of pozzolan in the binder, thus also decreasing the uncracked permeability.

It may be argued, however, that these measures may increase the risk for cracking because of the following reasons: (i) The measures described may also result in a more brittle concrete or in higher tensile stresses induced in the cover. (ii) The use of a very low w/b ratio, or the extensive use of pozzolans, may cause cracking of the fresh concrete as a result of plastic shrinkage, segregation of aggregates, retardation of early strength, etc. Furthermore, pozzolans in concrete will decrease the alkalinity of the pore water as illustrated in Fig. 23. The use of fibres as micro reinforcement, such as the micro reinforcement used for Densit at very low w/b ratios /46/, could in theory eliminate most of the cracking. However, little is known about the practical consequences from such a measure for structural concrete.

10.3.2 Research needs for a selective use of stainless steel in concrete

The following is a list of some research needs regarding the use of stainless steel in combination with ordinary steel in concrete:

The following topics must be considered in the evaluation of stainless steel qualities :

A) Critical chloride concentrations for initiation of pitting corrosion in concrete at various steel potentials and hydroxide concentrations.
  - unwelded
  - at weld joints of various types
  - at ordinary steel close to the weld joint

B) Ability of the steel to serve as a cathode in concrete
  - unwelded
  - welded, may welding affect the cathodic ability close to the weld joint?
  - welded connections to ordinary steel, should be similar as compared to welded connections to stainless steel

C) Passive steel potentials in concrete
  - stainless steel
  - stainless steel in metallic contact with ordinary steel
  - influence of various types of weld joints

D) Influence of various binders and micro climates on A-C)

E) Mechanical properties
  - stainless steel
  - combinations of stainless and ordinary steel

F) Cost effectiveness
  - materials
  - inspection
  - service life

10.4 Research needs regarding the critical chloride concentrations for ordinary steel in concrete

The points A-D) in the previous paragraph apply also for ordinary steel in concrete. Still very few reliable data are available for ordinary steel in long term field exposed concrete. Field and laboratory data must be evaluated with respect to passive potentials, the microstructure at the steel-concrete interface, free chloride and hydroxide concentrations. The relationship between steel potential and oxygen availability as influenced by the moisture state and the oxide layer at the steel should be studied more in detail for reinforced concrete.

Procedures for accurate measurements of free chloride, hydroxide and oxygen concentrations in modern high quality concrete are essentially lacking.

The most easy task is probably to collect and register reliable passive steel potentials in concrete, if error sources such as junction potentials are controlled. This can possibly be achieved by the use of cast-in reference electrodes.

10.5 Research needs regarding models for chloride, hydroxide, moisture and oxygen transport in concrete

Models for the combined transport of salts, hydroxide and moisture in concrete exposed in various environments are still lacking. The most easy environment to model - submerged concrete - is not a critical environment for reinforcement corrosion in concrete of reasonable quality. Other, more complex environments are much more difficult to model as compared to the submerged zone.

A model for the combined transport of chloride, hydroxide and moisture in concrete exposed in various environments must consider micro structural changes such as the effect of cracks and surface sealing. The most important environments to consider are probably concrete exposed to various deicing salts such as sodium and calcium chloride, and various acetate salts. Calcium Magnesium Acetate (CMA) may for instance introduce a surface sealing effect, due to the magnesium content.

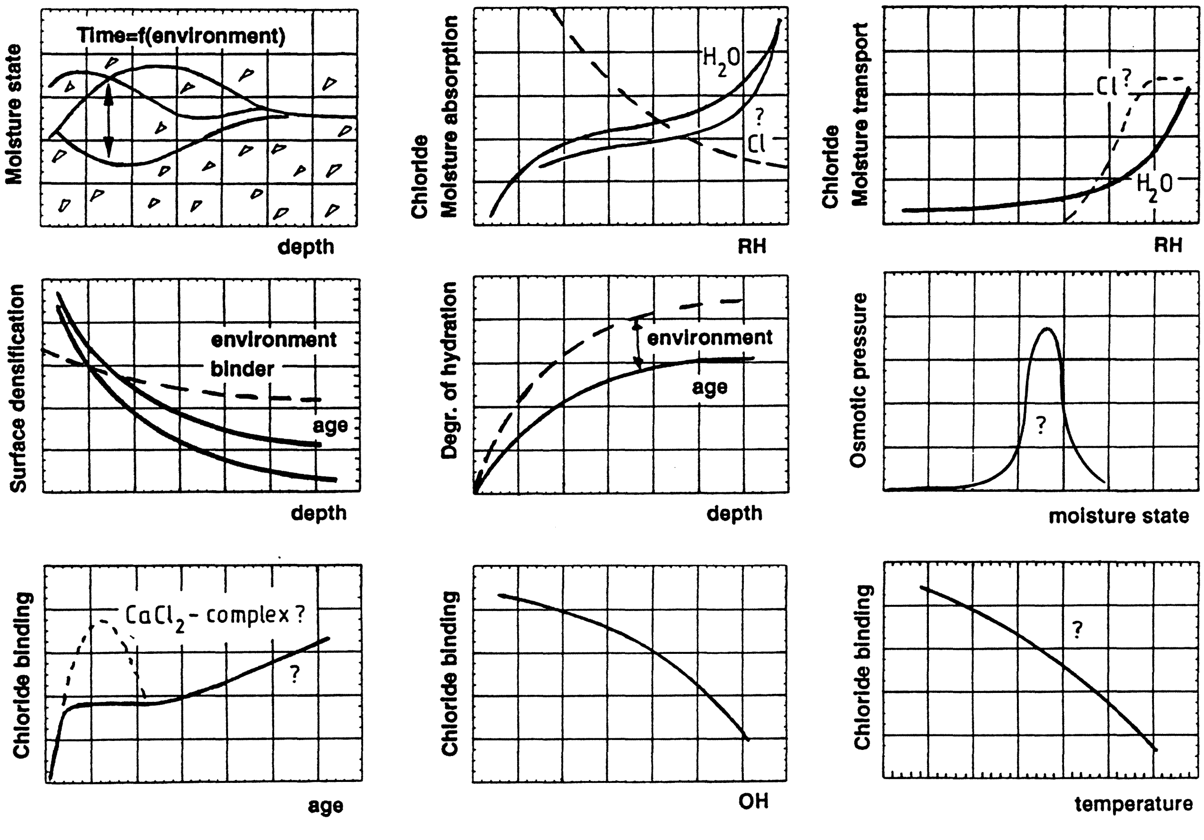


Fig. 69. Some hypothetical or known relationships influencing the transport of chloride, hydroxide and moisture in concrete.

In Fig. 69, some relationships, hypothetical or known, are illustrated as influencing the transport of chloride, hydroxide and moisture in concrete, as discussed by Fagerlund, Tuutti and Hedenblad /128/.

Furthermore, the synergistic effects of freezing and thawing on chloride transport and on propagating reinforcement corrosion can be modelled in a more accurate way as described by Fagerlund, Somerville and Tuutti /65/. Deicing salts may cause significant scaling that reduce the cover and thereby the initiation time for corrosion.

10.6 Research needs regarding experimental methods for systematic studies of pore solution chemistry

An accurate and reliable method for analysing the pore solution composition in modern semi dry, low w/b ratio concrete is essential for accurate measurements of threshold levels for corrosion initiation, and for detailed studies of ion transport in concrete.

10.7 Research needs for the characterisation of environmental aggressiveness in various micro climates

Chloride penetration profiles have been found to vary with orders of magnitudes within a given field concrete structural member. Apparently, the effect of local variations in the micro climate have a strong impact on the chloride penetration.

Therefore, it is most important to understand and quantify the effects of varying micro environmental loads on chloride, hydroxide, moisture and oxygen transport in field exposed concrete. It has been suggested that these effects may be described reasonably accurate by the time of wetness and the salt deposition rate /53,57/.

10.8 Research needs regarding long term field data on steel potentials, concentration profiles of chloride and hydroxide, and moisture state

Detailed field data are essential for the development of reliable models for chloride, hydroxide, moisture and oxygen transport in concrete. At present, field data may provide some empirical relationship to be used in the absence of accurate scientific models, as previously discussed in Chapters 8-9.

However, most long term field data available today are very difficult to use for service life predictions, since they are derived from a large variety of micro climates and concrete types, without detailed information on the micro environmental load and the concrete micro structure. A standard procedure for the collection of samples, analysis of important parameters, and reporting, is necessary, as suggested by Poulsen /115/.

11. TESTS OF THE EFFECT OF VARIOUS FACTORS ON THE TRANSPORT CHLORIDE, OTHER IONS AND MOISTURE IN CONCRETE

11.1 General

Selected topics regarding the transport of chloride, other ions and moisture into concrete are discussed more in detail in this chapter.

Chlorides are transported in concrete by means of diffusion, permeation due to overpressure and convection /77/. Concrete structures exposed to the marine environment or to deicing salts are frequently subjected to cyclic wetting and drying in the splash zone and the atmospheric zone. Traditionally, however, diffusion is regarded as being the dominating mechanism for chloride transport in high quality, concrete with low water to binder ratio. Since capillary transport, though a much more rapid process compared to diffusion, is minimised by the low capillary porosity in modern concrete with w/b ratios less than about 0.40, the capillary transport is usually neglected.

In this chapter all water to binder ratios have been calculated using activity factors as follow: Silica fume activity factor 1.0, fly ash activity factor 0.3.

11.2 Some laboratory studies of chloride permeability in concrete

11.2.1 General

Most laboratory testing of chloride permeability of concrete involves accelerated and simplified exposure conditions, such as the use of an electrical field or immersion in very strong chloride solutions. Such laboratory testing produces some permeability-related results, which are only valid for that specimen at the testing age and the specific exposure conditions used. Most of the experimental data from such laboratory tests are not useful for reliable service life predictions, without careful calibration against results from long term field exposure at relevant conditions.

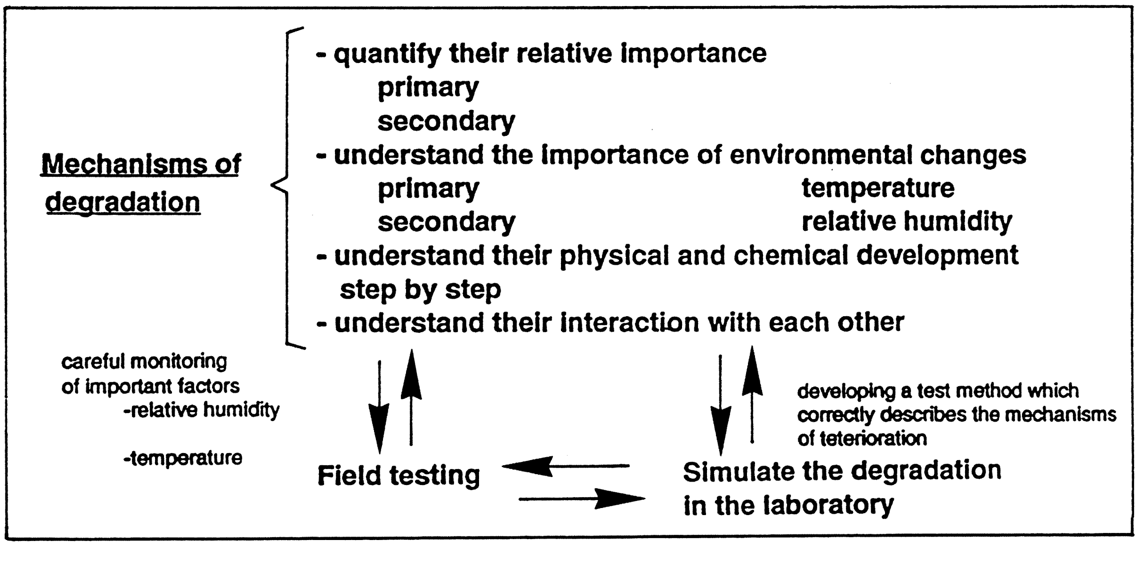


Fig. 70. General procedure for the development of testing methods for service life prediction, derived from recommendations by CIB/RILEM and ASTM /79-80/.

General procedures for the development of testing methods for service life prediction, by simultaneous field and laboratory testing, has been presented by CIB/RILEM and ASTM /79-80/, as illustrated in Fig. 70.

11.2.2 Accelerated laboratory testing of effective chloride diffusivity

Several accelerated testing methods for concrete chloride permeability are available internationally, as reviewed by Tang and Nilsson /83/. The most widely used is probably the AASHTO T277-83 method /81/, where an electrical field is applied across the concrete and the total charge passed through after 6 hours of testing is measured. It is then assumed that the total charge passing through the concrete relates to its chloride permeability. However, as reviewed by Arup et. al. /133/, the recording of the total current passing through concrete is not a function of the chloride flux or chloride mobility, since also other ions carry electrical charge. A simple resistivity test of concrete would reveal similar information as the AASHTO T277-83 test.

Recently, Tang and Nilsson developed a more simple rapid electrical field method, which they called the "Chalmers method", being able to separate the chloride ion transport from the transport of other ions. An electrical field is applied to accelerate a chloride front into the concrete. The penetration depth of the chloride front for a given exposure time, temperature and potential is related to the chloride diffusivity of the concrete /84/.

The Danish immersion test APM 302 for evaluating the chloride penetration into bulk concrete involves the immersion of cut concrete surfaces into a strong (17 % by weight) solution of NaCl. After about 35 days of exposure, the acid soluble chloride profile is determined by consecutive grinding of concrete powder samples taken from increasing depths from the exposed concrete surface. The effective chloride diffusivity is estimated by fitting the experimental chloride profile to the theoretical profiles calculated from Fick´s second law of diffusion /86/.

In Fig. 71, effective chloride diffusivities from the "Chalmers method" are compared to the corresponding values from the Danish immersion test APM 302 /85/.

Apparently, the correlation between the methods is good for normal concrete. But the electrical method seems to underestimate the effective chloride diffusivity for concrete with large amounts of pozzolans as compared to the immersion test. The effect of the electrical migration of ions on chloride binding is mainly unknown. The chloride binding during the test may be different for different types of binders.

However, none of these chloride diffusivity tests will alone predict the long term chloride transport into a real concrete structure in the field being influenced by changes in the concrete micro structure and the moisture state, which is in turn controlled by the micro climate.

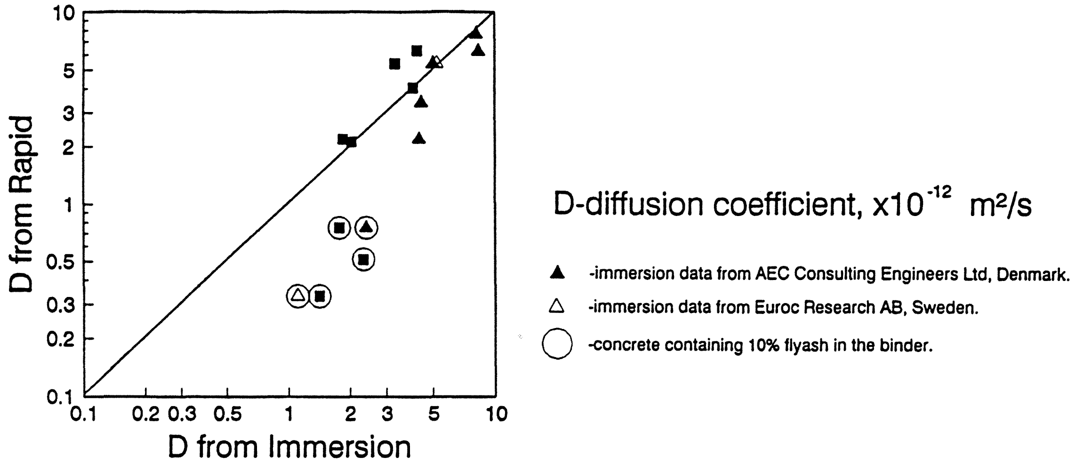


Fig. 71. Comparison of effective chloride diffusivities determined by the Chalmers electric field method and the Danish immersion test APM 302 /85,86/.

11.2.3 Tests of factors affecting the chloride penetration in a laboratory immersion test

Sergi et. al., Chatterji, Rombén, Yonezawa /75,87,88,89,120/ and many others have indicated the complex nature of the process of chloride ions penetrating into concrete pore solution and interacting with hydroxyl-, calcium-, potassium-, sodium-, and sulfate ions there.

Furthermore, the pore solution is affected by an electrical double layer, apparently affecting the diffusion properties of ions entering and leaving the pore solution. Chatterji stated that ion transport through cement based materials can be described only by using a combination of Nernst, Nernst-Planck and the electrical double layer diffusion processes /88/.

Bearing these considerations in mind, laboratory immersion tests were carried out by Tang /90/ and Sørensen /91/ in order to evaluate the relative importance of (i) the exposure temperature, (ii) the co-diffusion, the counter-diffusion and other interactions of sea water ions, on the chloride penetration into the concrete. Some results are shown in Fig. 72, as presented by Tang /90/ and Sørensen /91/.

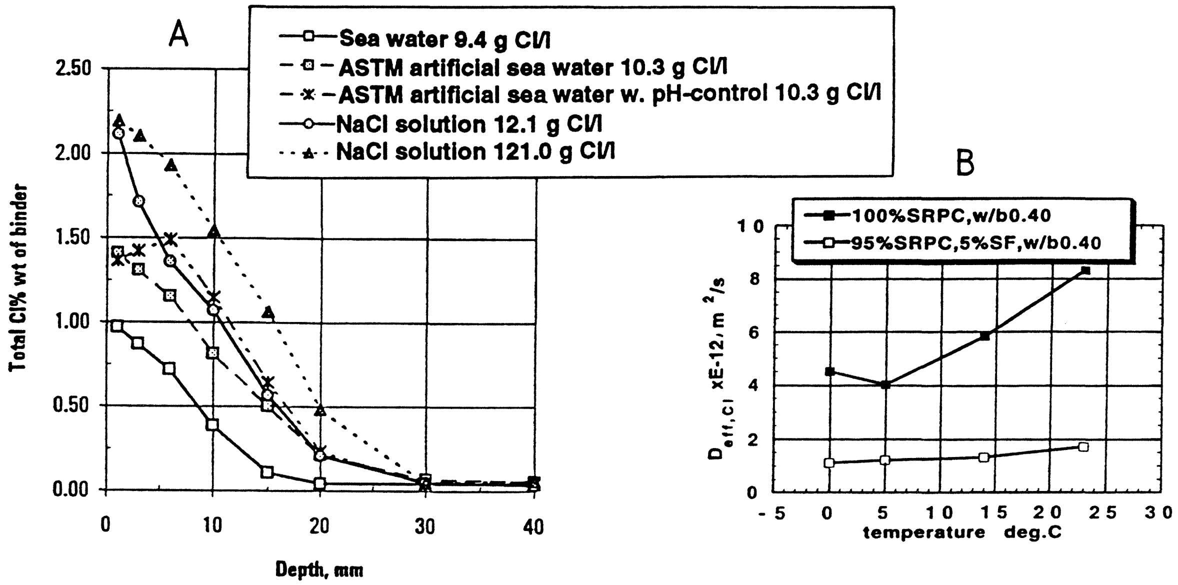


Fig. 72. Chloride penetration in different solutions and at different temperatures (A): The effect of composition of the chloride solution on chloride penetration into Portland cement concrete of w/b 0.35 submerged for 12 months. (B): The effect of exposure temperature on the effective chloride diffusivity as evaluated by the Danish immersion test APM 302 /91/.

11.2.4 Tests of the effect of atmospheric exposure on chloride penetration

As a part of the studies described in section 11.2.3, Tang also studied the effect of drying on the chloride penetration under fairly well controlled laboratory conditions /90/. Figs. 73-75 illustrate the effect of external moisture variations on the chloride penetration into concrete as presented by Tang /90/. In these tests the most rapid chloride penetration took place just above the water line, thereby indicating the relative importance of chloride transport due to the wick effect.

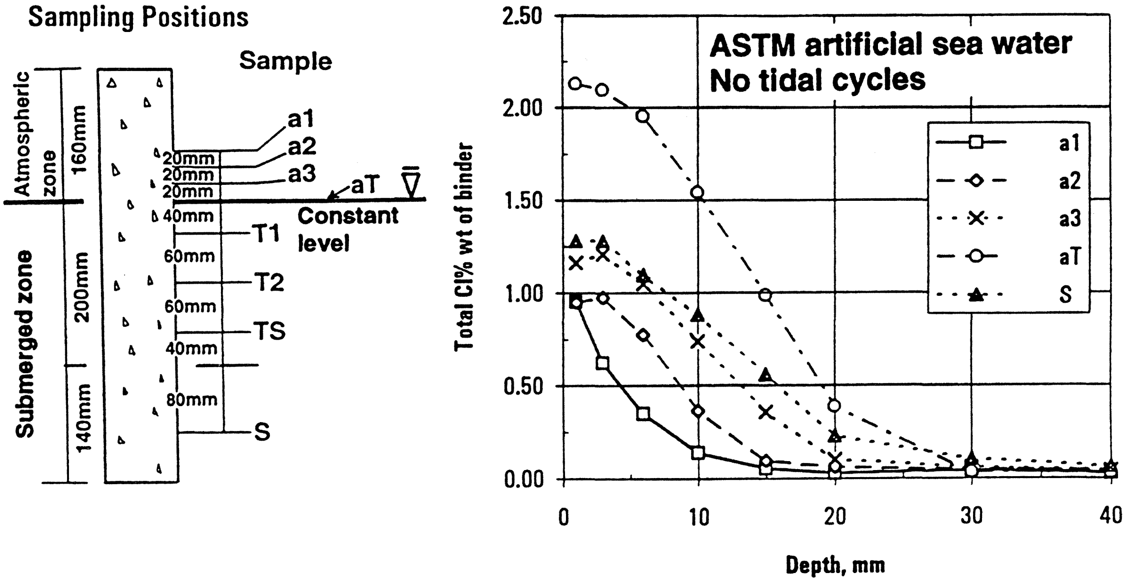


Fig. 73. The effect of extensive drying on chloride penetration into Portland cement concrete of w/b 0.35 exposed for 12 months in artificial sea water, no tidal cycles /90/.

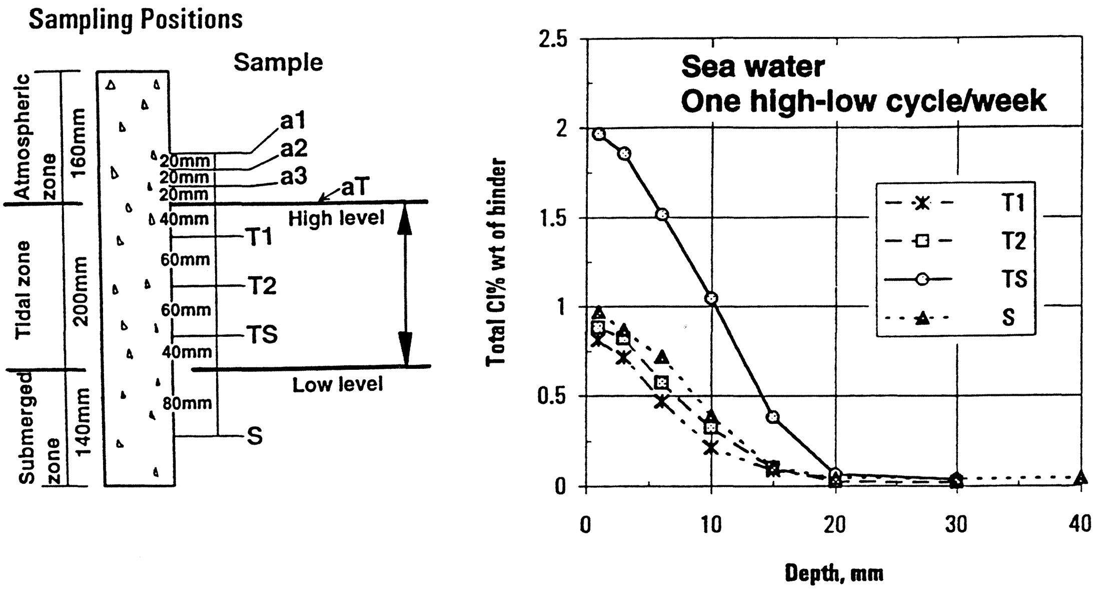


Fig. 74. The effect of the micro climate and the position of the sampling on the chloride penetration into Portland cement concrete of w/b 0.35 exposed for 12 months in natural sea water, 1 tidal cycle/week /90/.

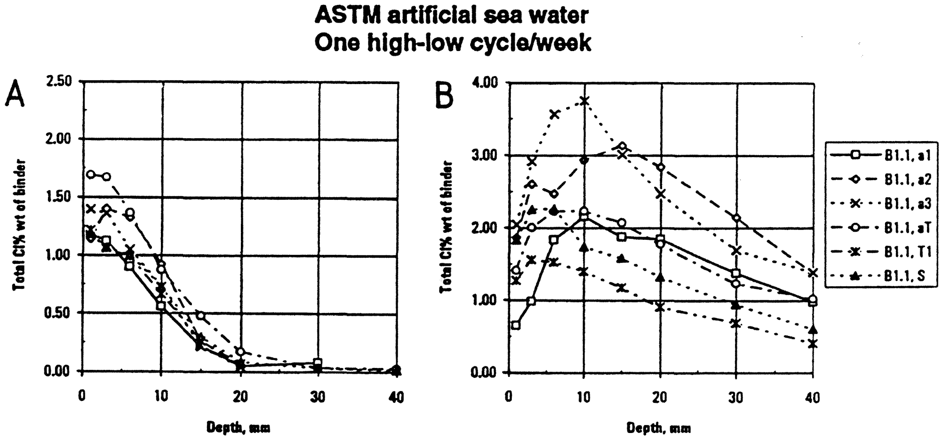


Fig. 75.The effect of the micro climate and the position of the sampling on the chloride penetration into Portland cement concrete of w/b 0.35 (A) and w/b 0.75 (B), exposed for 12 months in artificial sea water, 1 tidal cycle/week /90/.

Janz and Johannesson /58/ studied the same topic and the effect of improper curing on the chloride penetration into concrete cylinders of w/b 0.35-0.55, exposed to various cyclic and non-cyclic saline exposure. (Cyclic wetting in a 3% sodium chloride solution at 20°C and drying at 20 °C and 50-60% RH.) Similar as Tang did, they found a large effect of cyclic exposure on concrete with high w/b-ratios, but sometimes a significant effect also on concrete with w/b < 0.40 /90,92/.

Apparently, cyclic wetting and drying facilitates an initially rapid carbonation of the concrete surface, besides drying and some salt accumulation. Therefore, the surface conditions in such treatment are quite different from submerged exposure.

In a short term test such surface effects will affect a major part of the concrete volume that is penetrated by chloride. Thus they are considerably affecting the chloride profile and any transport coefficient calculated from it. In the long term, however, chlorides will penetrate deeper and deeper into the bulk concrete that is less affected by surface effects. Thus, such surface effects on dense concrete may be considered being less important in the long run, if the surface effects does not significantly affect the overall concrete durability such as the frost resistance.

The very large variations in chloride penetration found in both laboratory and field studies at various cycles of drying and saline wetting indicate a very complex relationship between the concrete moisture state, the chloride load, the micro structural changes (including degradation) and the chloride transport. An important step in order to understand and model the chloride penetration in a semi-dry concrete would therefore be to study and model the simultaneous transport of salts and moisture in the concrete, as outlined by Hedenblad /92/. Moisture transport data derived from concrete exposed to non-saline environment is probably not applicable, since salts affect the moisture conditions.

11.2.5 Tests of a method for studying the concrete surface permeability

A slight modification of the direction of exposure used in the rapid chloride permeability method developed by Tang /84/, made the method suitable for studying concrete surface permeability /112/, as illustrated in Fig. 76. Concrete surface permeability testing involves the migration of a chloride front under an electrical field acting parallel to the concrete surface of interest.

As for the normal procedure for the "Chalmers Rapid Method", the chloride penetration depth at the concrete surface as well as in the bulk, can be assumed to be a function of the concrete permeability. Thus, a chloride diffusivity can be calculated, using certain assumptions of the effect of the pore solution composition on the chloride migration resistance.

The chloride penetration profile thus represents a relative measurement of the concrete surface permeability as compared to the bulk permeability, which in turn may be obtained by a standard laboratory chloride permeability test.

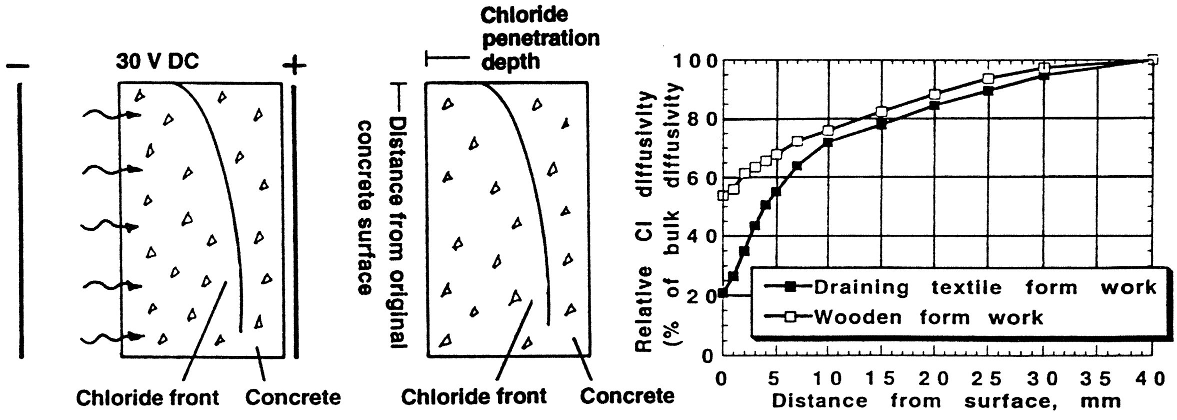


Fig. 76. Schematic illustration of the procedure for studying the concrete surface permeability by the "Chalmers Rapid Method" /112/.

The concrete surface permeability was tested on unexposed concrete taken from the New Öland Bridge in Sweden. Tests were made on concrete cast against a draining textile form work as compared to a conventional wooden form work. The effect of form work type on the concrete surface permeability is indicated to the right in Fig. 76.

11.3 Studies on the effect of crack sealing on the chloride transport into concrete

Concrete always contains cracks to some extent. In section 7.4, a general discussion of the negative effects of cracks in concrete was undertaken. Here some experimental findings regarding crack permeability are discussed.

Thermal cracking was observed at a full scale test of various designs for the concrete columns at the New Öland Bridge in Sweden. After four years of exposure, the thermally cracked column was studied with respect to chloride ingress into cracked and uncracked parts of the structure. Thermal cracks observed by thin section microscopy and scanning electron microscopy were typically < 10 microns wide, although a few larger cracks, up to 300 microns wide, were occasionally observed. A typical set of total chloride profiles from submerged cracked and uncracked concrete is shown in Fig. 77 /31/.

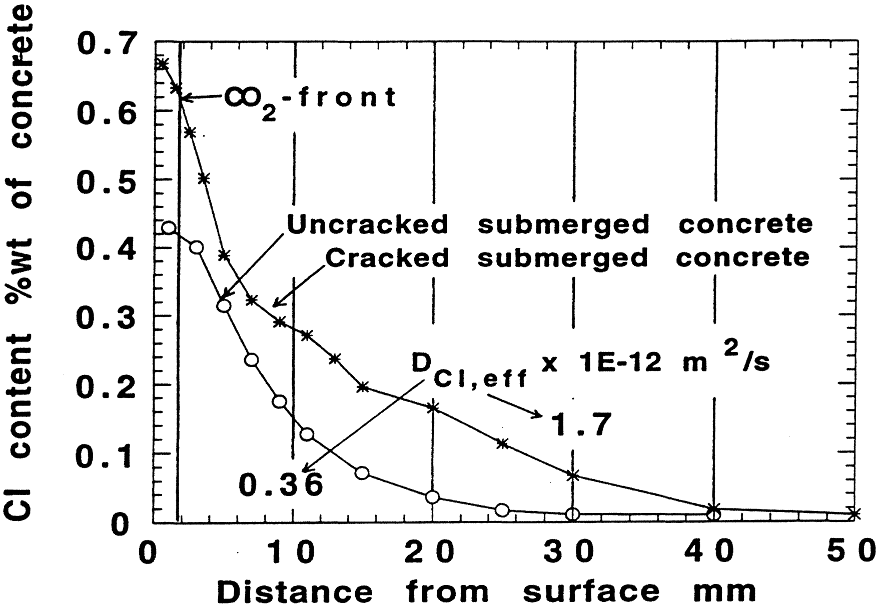


Fig. 77. The effect of thermal cracking on the total chloride profile found in uncracked and cracked concrete after 4 years of submerged marine exposure. Thermal cracks observed were typically < 10 microns wide, although a few larger cracks, up to 300 microns wide, were occasionally observed /31/.

An investigation of minerals and salts found in the cracks by means of thin section microscopy, SEM -EDAX and XRD analysis, revealed several examples of self healing of cracks, by the formation of deposits containing brucite and calcium carbonate mainly. Unfortunately, pictures from the thin section studies and the SEM studies were not suitable for ordinary and white printing. However, the schematic sketch in Fig. 39 corresponds very well with the experimental results.

Thus, the indications from this study are: (i) The self healing capacity of submerged marine Portland cement concrete resulted in significant clogging of cracks less than 0.3 mm wide. The clogging was predominant at the crack surfaces, apparently because water movement did not occur inside deeper cracks. (ii) In spite of the extensive crack sealing, cracks up to 0.3 mm width significantly affected the chloride ingress as evaluated by a chloride profile, see Fig. 77.

Similar observations have been made by Espelid /78/, who found chlorides on large depths inside a crack system. These cracks had developed after several years of marine exposure of a high performance lightweight off-shore concrete, with no visible cracks after the first years of exposure at Bergen, Norway.

The accelerating effect on the long term chloride transport into concrete caused by a large amount of small cracks may as a first and simple approximation be accounted for by the calculation of an "effective cover thickness", being the total cover thickness minus a calculated "effective crack depth", see Fig. 68. If chloride profiles obtained experimentally exist from cracked and uncracked concrete exposed in a similar way, the "effective crack depth" may be estimated using chloride profiles from uncracked and cracked concrete as illustrated to the right in Fig. 68.

It is then assumed that an initially rapid chloride penetration at later ages approaches the same penetration rate as in an uncracked concrete, provided that significant time dependent crack propagation is absent. The long term chloride penetration rate estimated in uncracked concrete could be used in combination with the smaller effective cover size, thus taking the cover reducing effect of cracks into account.

11.4 Tests of the effect of the pore size distribution on the chloride permeability in concrete

11.4.1 General

The effect of the pore size distribution was studied for marine field exposed concrete at Träslövsläge field station, in terms of varying water to binder ratios and varying silica fume and / or fly ash content in the concrete mix design.

11.4.2 Tests of the effect of the water to binder ratio

The effect of a decreasing water to binder ratio after 2 years of marine exposure is illustrated for Portland cement concrete in Fig. 78, and for a binder composed of 95% Portland cement and 5% silica fume in Fig. 79.

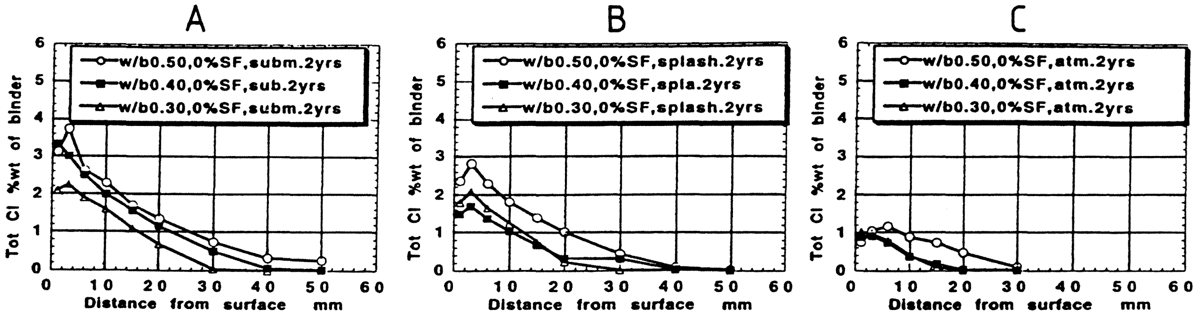


Fig. 78. The effect of a decreasing water to binder ratio on chloride penetration into concrete made with Swedish sulfate resisting, low alkali Portland cement after 2 years of marine exposure. (A): Submerged-, (B): Splash-, (C): Atmospheric zone /92/.

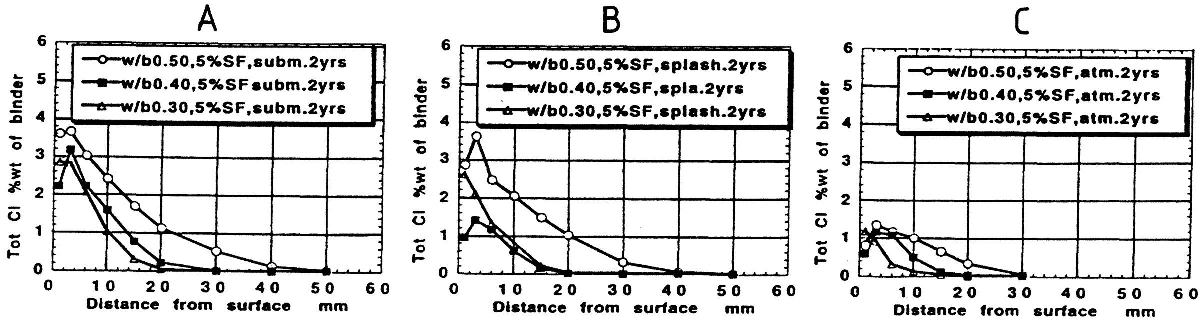
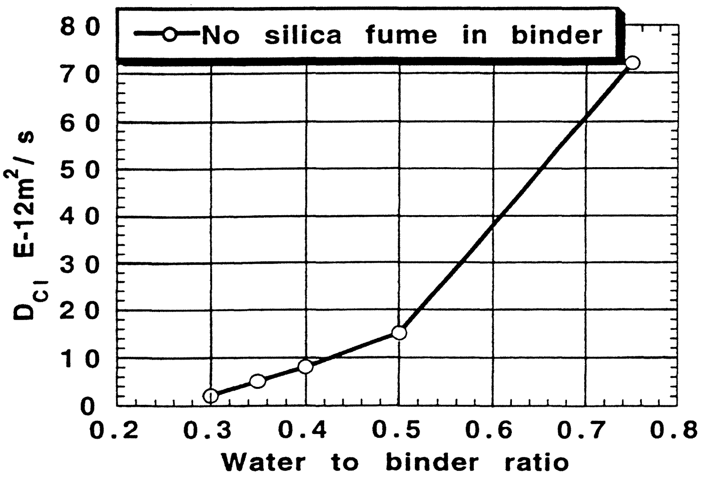


Fig. 79. The effect of a decreasing water to binder ratio on the chloride penetration into concrete made with 95% of Swedish sulfate resisting, low alkali Portland cement and 5% silica fume, after 2 years of marine exposure. (A): Submerged-, (B): Splash-, (C): Atmospheric zone /92/.

The effect of a decreasing water to binder ratio on the measured chloride diffusivity in concrete measured by a laboratory bulk diffusion test is illustrated in Fig. 80. A similar trend as found for submerged field concrete was found in the laboratory testing.

Fig. 80. The effect of a decreasing water to binder ratio on the chloride diffusivity in concrete measured after 180-360 days of curing by a laboratory bulk diffusion test /93/.



11.4.3 Tests of the effect of silica fume and fly ash on the chloride penetration into concrete

In Fig. 81, the effect of replacing 0 to 10% of Portland cement with silica fume, on the chloride penetration is shown for concrete with w/b 0.40 after 1 year of marine exposure.

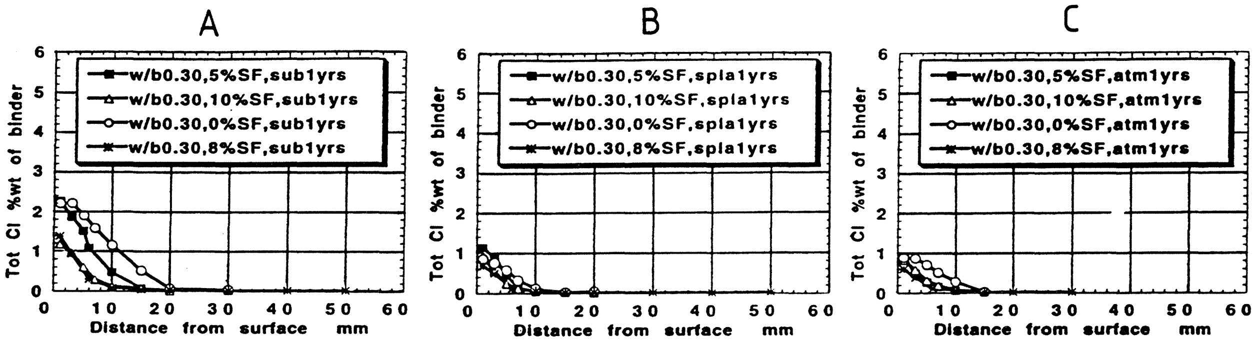


Fig. 81. The effect of replacing 0 to 10% of Portland cement with silica fume on the chloride penetration into concrete made with Swedish sulfate resisting, low alkali Portland cement of w/b 0.30, after 1 year of marine exposure. (A): Submerged-, (B): Splash-, (C): Atmospheric zone /92/.

The corresponding effect of silica fume on the measured chloride diffusivity obtained from (i) laboratory bulk diffusion test on concrete, (ii) field chloride profiles fitted to the theoretical profiles by Fick´s second law of diffusion, is illustrated in Fig. 82. A similar trend as found for submerged field concrete was found in the laboratory testing, although the diffusivities calculated from field testing are always smaller compared to the ones measured in the laboratory tests.

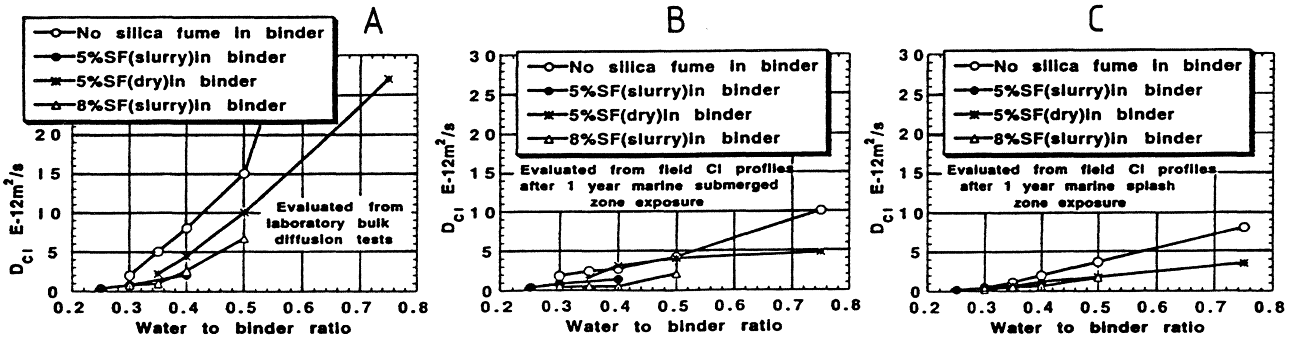


Fig. 82. The effect of silica fume in the binder on the chloride diffusivity measured in concrete, (A) by a laboratory bulk diffusion test, (B,C) by fitting field chloride profiles from the submerged- and the splash zone to the theoretical profiles by Fick´s second law of diffusion /93/.

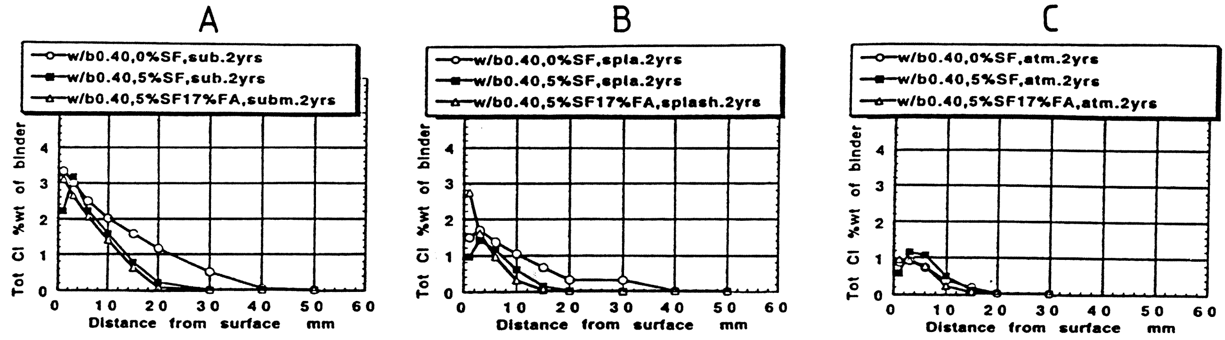


Fig. 83. The effects of replacing Portland cement with 5 % silica fume or 5 % silica fume + 17 % fly ash, on the chloride penetration into concrete made of Swedish sulfate resisting, low alkali Portland cement of w/b 0.40, after 2 years of marine exposure. (A): Submerged-, (B): Splash-, (C): Atmospheric zone /92/.

The effects of replacing Portland cement with 5 % silica fume or 5 % silica fume + 17 % fly ash, on the chloride penetration are shown in Fig. 83, for concrete w/b 0.40 after 2 years of marine exposure.

In Fig. 84, "effective chloride diffusivities" as evaluated from field chloride profiles from concrete exposed to the splash zone at Träslövsläge Field station, is illustrated together with similar data from real marine structures, taken from Fig. 52.

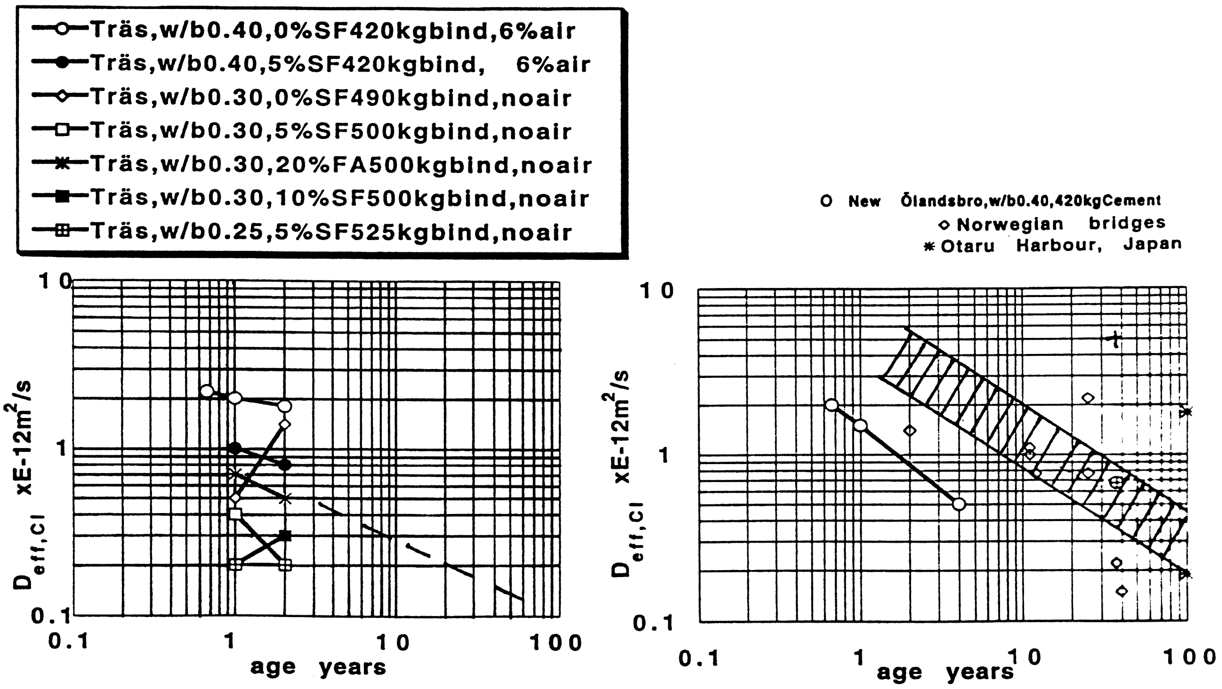


Fig. 84. "Effective chloride diffusivities" as evaluated from field chloride profiles from concrete exposed to the splash zone at Träslövsläge Field station /92/, are compared to similar data /67/ from marine structures.

11.4.4 A discussion of the effect of the workability

The effect of insufficient compaction as a result of bad workability on the chloride penetration was illustrated in Fig. 32. As indicated, a concrete with w/b 0.32 but with an insufficient compaction had a higher chloride permeability as compared to a crack free concrete of w/b 0.60. The theoretical benefit from a low water to binder ratio may be more than counteracted by an insufficient workability of the concrete. Therefore, excellent workability is a requirement for the production of concrete with a low chloride permeability.

The workability of concrete with a given w/b-ratio is affected by the type and amount of binder, the type and amount of water reducer/superplasticizer, and the type, shape and particle size distribution of the aggregates /61,94,95/.

Portland cements rich in C_3A (Tricalciumaluminate) and alkali generally consume more water in the initial cement hydration compared to Portland cements with a similar surface area but with low contents of C_3A and alkali. Portland cements with a high surface area are initially more reactive compared to the same cement ground to a smaller surface area. However, when compared to more early reactive cements, Portland cement with a low surface area and a low content of C_3A and alkali are also more sensitive to bleeding besides being more slow reacting, the latter causing a slower early strength development /61,94,95/.

The addition of a micro filler with a high specific surface will, if not increasing the early water consumption of the concrete, improve the concrete workability, uniformity and strength. Thus, the use of 5-8 % silica fume by weight of cement usually improves the concrete quality in terms of reduced bleeding, a more uniform micro structure and higher strength /61,94,95/.

Chemical admixtures such as air entrainers and superplasticizers have a dramatic influence on the fresh concrete properties, and therefore also on the concrete durability.

It is very important not only to consider workability after mixing the concrete, but also the loss of workability some 30-60 minutes after mixing. Naturally, it is also important to control properly the transport conditions and the duration between mixing and casting.

The use of a high amount of superplasticizer in order to compensate for a bad initial workability might ruin the concrete for several reasons:

(i) Superplasticizers accelerate ettringite formation at early ages in concrete containing sulfate resisting Portland cement. Since ettringite is a water binding mineral, an increased ettringite formation in the fresh concrete may cause rapid loss of workability. The effect of a melamine based superplasticizer on the formation of ettringite and gypsum in a Swedish sulfate resisting Portland cement paste of w/b 0.40 is shown in Fig. 85 (A), as measured by differential scanning calorimetry. The corresponding pore fluid chemistry, as measured by the method of pore solution expression, is shown to the right /98/.

(ii) Too much superplasticizer significantly retard the silicate reactions and thus the strength growth, especially so at low temperatures. As a consequence, the concrete becomes much more sensitive to drying and plastic shrinkage at early ages. The effect is further increased by an increased water evaporation rate from the fresh concrete caused by an extensive use of superplasticizers.

(iii) The dispersing action of superplasticizers will, if exaggerated, destroy the internal stability of the system of binder, aggregates and air voids. The hardened air entrained concrete might suffer from a bad frost resistance and a higher permeability, due to a non-uniform micro structure.

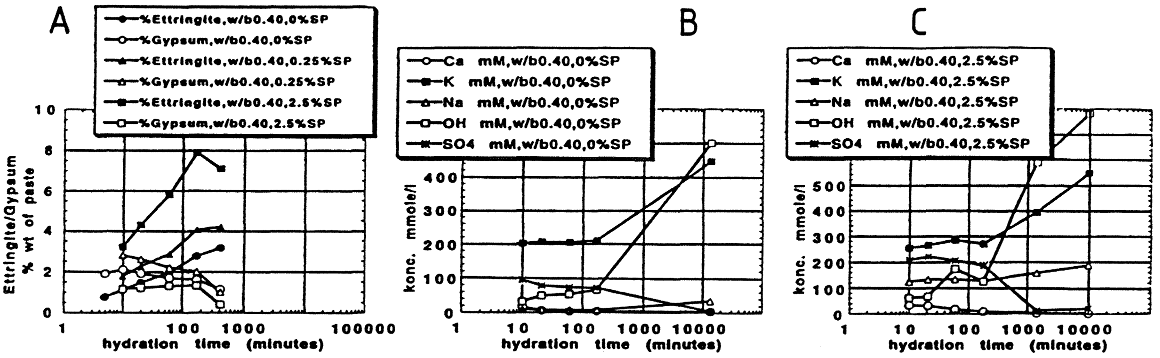


Fig. 85. The effect of superplasticizers. (A): The effect of a melamine based superplasticizer on the formation of ettringite and gypsum in a Swedish sulfate resisting Portland cement paste of w/b 0.40. (B,C): The corresponding chemistry of the pore fluid /98/.

The compatibility of Swedish sulfate resisting Portland cement with silica fume, a melamine based superplasicizer and a lignosulfonate based water reducer is indicated in Fig. 86. Note that different cements may perform different when combined with a given set of additives.

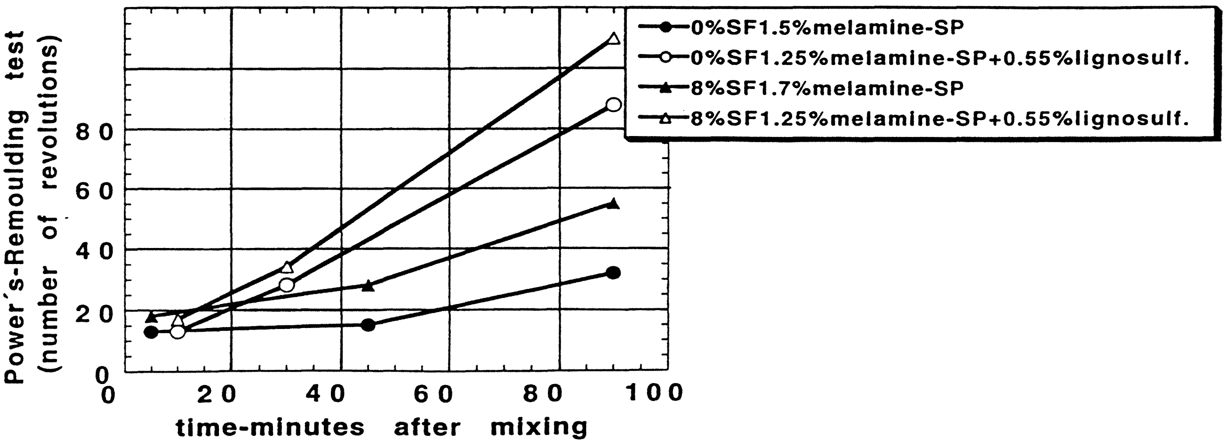


Fig. 86. The effect of silica fume and type of superplasticizer/water reducer on the consistency of a concrete of w/b 0.35 and with 400 kg binder/m^3 /61/. The concrete consistency was measured by Powers Remoulding test. A number < 40 indicates acceptable workability.

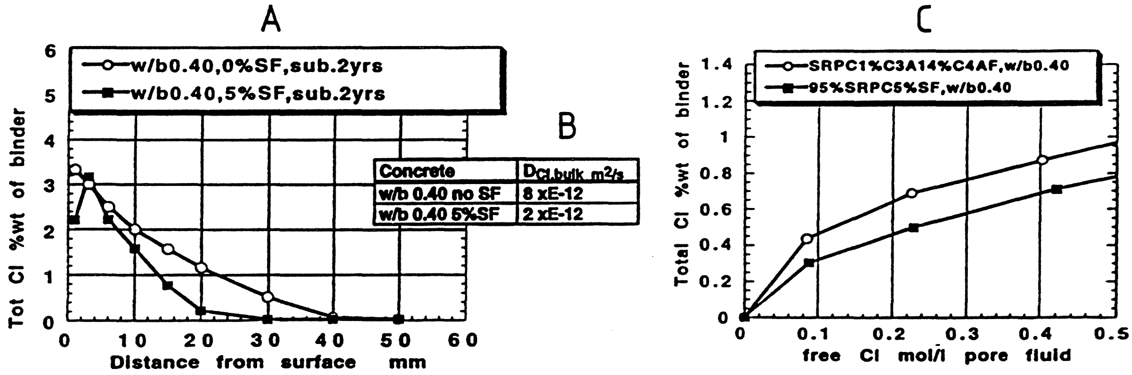
11.5 A discussion of the importance of chloride binding relative to the effect of the pore size distribution, on the chloride permeability of concrete

The chloride binding effect of the concrete binder affects the effective chloride permeability of the concrete, since a certain amount of diffusing chloride ions are removed from the concrete pore solution by the chemical and physical binding processes. The chloride binding capacity of a concrete with a given w/b ratio varies with the type of binder, the interaction with other ions and the chloride concentration. As a consequence, chloride binding has a certain time dependency for a given concrete mix design in a given environment, as indicated by Tuutti, Nilsson and Byfors among others /8,9,55,69,71/.

An experimental study of the influence of various binders on the chloride binding and chloride permeability was carried out by Sandberg and Larsson /69/. The study involved (i) documentation of the chloride binding capacity of cement pastes made of various binders immersed in synthetic pore solutions with various concentrations of chloride and hydroxide, (ii) evaluation of the relative effect of chloride binding when compared to the effect of the pore size distribution, as controlled by introducing silica fume into the binder.

Some results from the first part of the study are illustrated in Fig. 19. As seen in Fig. 19, cement pastes containing 5% silica fume indicated less chloride binding capacity when compared to pastes without silica fume, for a given w/b ratio and alkalinity.

In the second part of the study, these results regarding chloride binding were compared to chloride profiles and laboratory measured effective bulk chloride diffusivities measured in field concrete, exposed at Träslövsläge Field Station and having similar binder compositions as in the first part.



Concrete	$D_{Cl,bulk}$ m²/s
w/b 0.40 no SF	8 xE-12
w/b 0.40 5%SF	2 xE-12

Fig. 87. Total chloride profiles (A) measured in submerged concrete after two years of marine exposure at Träslövsläge Field Station, and effective chloride diffusivities measured by laboratory testing of the same bulk concrete (B) /92,93/, are compared to the laboratory chloride binding capacity found for each binder (C) /69/.

As indicated in Fig. 87, the silica fume concrete was found to be much more resistant to chloride penetration as compared to the concrete without silica fume. Thus, when comparing chloride binding data on silica fume pastes with the corresponding chloride penetration data on silica fume concrete, the pore size distribution may be considered as being a more important parameter as compared to the chloride binding.

On the other hand, silica fume substantially reduces the pH of the pore solution as compared to a similar concrete with no silica fume, see Fig. 23. Furthermore, considering the effect of the alkalinity on chloride binding of a given binder, see Fig. 19 (B), one may argue that the data in Fig. 19 (A) are somewhat misleading, since they were derived from samples conditioned to a nearly constant alkalinity.

Anyhow, detailed knowledge on the chloride binding capacity of field exposed concrete is very important for several reasons such as (i) the prediction of chloride penetration rate in the concrete, (ii) the translation of frequently measured total chloride contents in the concrete into concentrations of free chlorides in the concrete pore solution; It is the concentration of free chloride ions and not the total chloride content which influences the initiation of reinforcement corrosion.

11.6 Tests of the effect of cement fineness on the chloride penetration into concrete

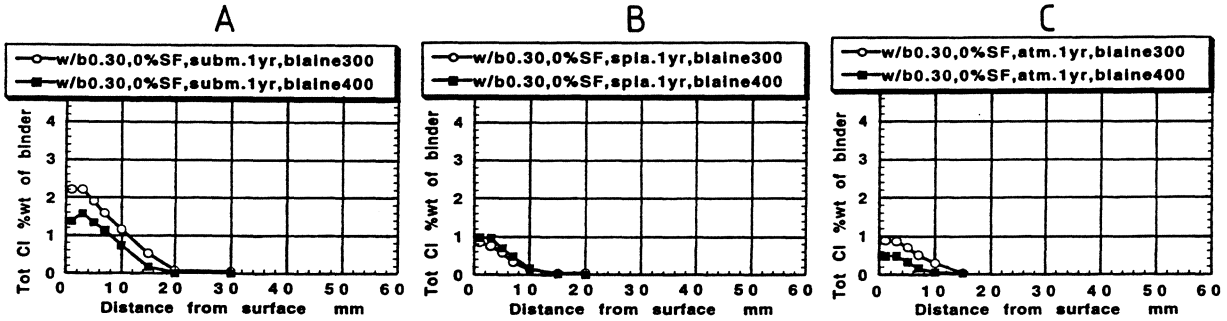


Fig. 88. Total chloride profiles measured in high performance concrete of w/b 0.30 (no silica fume in the binder) after one year of marine exposure at Träslövsläge Field Station, (A): Submerged-, (B): Splash-, (C): Atmospheric zone /69,96/.

The effect of Portland cement fineness was studied at Träslövsläge Field Station by comparing field chloride profiles in concrete after one year of exposure, for w/b 0.30 with either the coarser "Anläggningscement" (Blaine surface 300 m^2/kg) or the finer "P400" (Blaine surface 400 m^2/kg). The results are shown in Figs. 88-89 /69,96/.

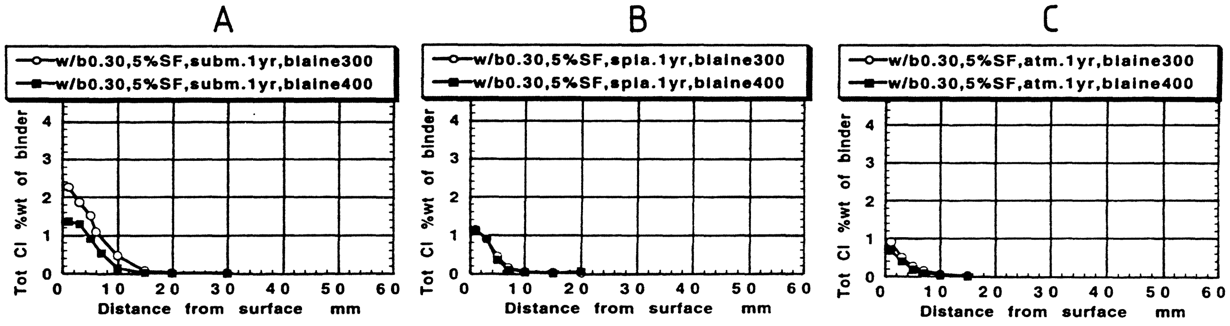


Fig. 89. Total chloride profiles measured in high performance concrete of w/b 0.30 (5 % silica fume in the binder) after one year of marine exposure at Träslövsläge Field Station, (A): Submerged-, (B): Splash-, (C): Atmospheric zone /69,96/.

The positive effect of a finer ground cement on the resistance to chloride penetration of concrete has been noted elsewhere /129/. The effect is not likely to be explained by a difference in the degree of cement hydration, since the concrete was cured for 14 days prior to exposure. A that age the difference regarding the degree of cement hydration is very small. However, higher long term strengths of concrete have also been observed when using a finer ground cement for a given concrete quality /97/. It is possible that a well dispersed finer ground cement in concrete may contribute to a more uniform micro structure, thereby affecting the chloride penetration.

The following should be noted: (i) The apparent benefit in the resistance to chloride penetration by using a finer cement as indicated in Figs. 88-89 is often difficult to realise in practise, due to higher initial hydration for the finer ground cement. A finer ground cement generally consumes more mixing water or plasticizing admixtures for a given consistency of the fresh concrete, as compared to a coarser ground cement of the same chemical composition. Therefore, fresh concrete problems may arise as a consequence of an increased addition of superplasticizer.

ii) The potentially negative effect on workability by increasing the initial cement hydration by the use of a finer cement may be counteracted by optimising the proportioning of the mix design. In other words, small amounts of a finely ground cement in the binder fraction may result in an improved homogeneity, when compared to the standard use of a coarse cement and a micro filler (silica fume).

Several promising indications have been found in a joint project by Cementa AB and Tyréns AB /97/. Such "micro proportioning" of the binder in high performance concrete may result in improved early strength and improved resistance to chloride penetration, indicating a potential benefit for the precast concrete industry.

11.7 Studies of the effect of moisture state on chloride transport in concrete

11.7.1 General

As previously discussed, a relationship between moisture transport and chloride transport in concrete is likely to exist. Here some results and some discussions regarding combined moisture and chloride transport in concrete are presented.

11.7.2 Field studies of sea water and moisture transport in concrete

Field studies of the transport of sea water and moisture into semi dry concrete has been undertaken by Chalmers and Lund Institute of Technology /99,100/. Although a larger spread in experimental data was observed for field exposed marine concrete as compared to normal measurements in normal indoor concrete floors, a general relationship between the moisture profile and the chloride profile was indicated for concrete with w/b less than 0.40, as illustrated in Fig. 90.

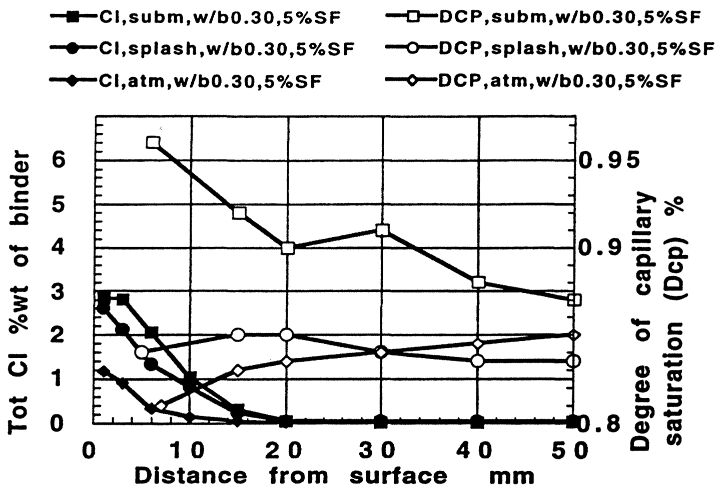


Fig. 90. Moisture and chloride profiles found in marine concrete of w/b 0.30 after 2 years of field Exposure at Träslövsläge /92,99,100/ The moisture profiles represent mean values of several measurements. Since the spread in the results was high, the moisture profiles should only be regarded as indicative.

After 2 years of field exposure, the moisture gradient had more or less disappeared for 10 cm thick concrete slabs with w/b 0.50. As expected, however, the moisture levels were higher in submerged concrete as compared to concrete exposed to the atmosphere, see Fig. 91.

As reported by Persson /101/ among others, concrete with a w/b ratio less than 0.40 may remain non-saturated with water in the inner part of the concrete even after years of submerged exposure, due to the self dessication of the binder. At present it is not known if such high performance concrete eventually will become water saturated when submerged for a long time, or if the moisture profile indicated in Fig. 90 will stop at a certain level, as balanced by a reduced surface permeability and remaining water binding by the hydrating cement.

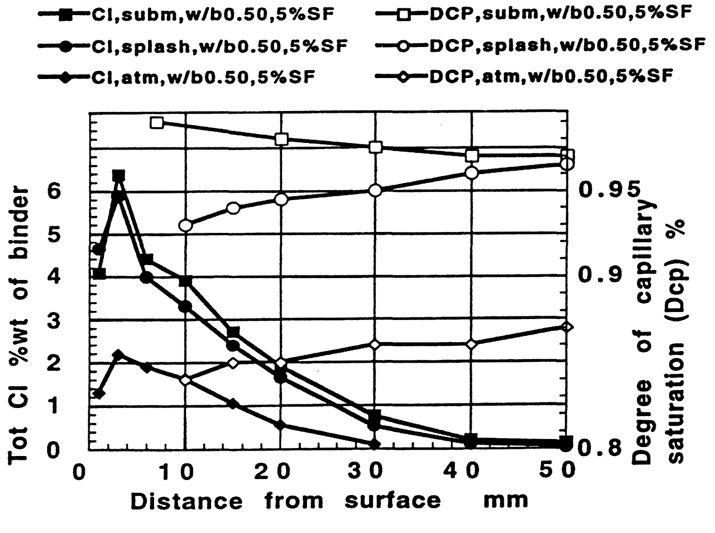


Fig. 91. Moisture and chloride profiles found in marine concrete of w/b 0.50 after 2 years of field Exposure at Träslövsläge /92,99,100/.

11.7.3 A discussion of water and chloride suction into submerged concrete

As discussed by Volkwein /102/, shrinkage due to the binder hydration in concrete may cause suction of external water into concrete. Considering a typical Portland cement marine concrete of w/b 0.40, anhydrous cement originally occupy about 44.3 % of the total volume of anhydrous cement + mixing water. When fully hydrated, the cement paste occupy a volume which is 89 % of the original volume of anhydrous cement + water, the remaining 11 % is empty pores /103/, creating a suction according to Volkwein as schematically illustrated in Fig 92.

In other words, 100 grams of unhydrated cement (specific gravity about 3.14) + 40 grams of water initially occupy a volume of 71.85 cm^3. When fully hydrated, the cement paste occupy a volume which is 89 % of the original volume of anhydrous cement + water, i.e. 63.94 cm^3, the remaining volume of 7.90 cm^3 being empty pores. Thus, 100 grams of unhydrated cement could as a maximum suck in approx. 8 grams of sea water with a maximum chloride concentration of 1.94 % by weight, resulting in an average level of 0.15 % sucked-in chloride by weight of cement.

Thus, the effect of hydration suction is marginal on the long term *average* chloride content in submerged marine concrete. On the other hand, the strong filter effect of the binder in a low w/b concrete as indicated by Volkwein, will remove chlorides from the sucked-in sea water close to the concrete surface. Thus, an accumulated chloride profile with similar shape as a diffusion profile, will develop as controlled by the pore size distribution and the connectivity of the concrete.

Clearly, the effect of suction due to hydration on a measured chloride profile may be significant. The effect probably depends on the size of the submerged concrete member, since a large concrete member will provide larger volumes to be filled by suction. Thus, relatively more chlorides will be filtered and deposited in close to the concrete surface. In other words, the cover thickness needed to prevent sucked chlorides from being deposited at the reinforcement would be related also to the thickness of the concrete member.

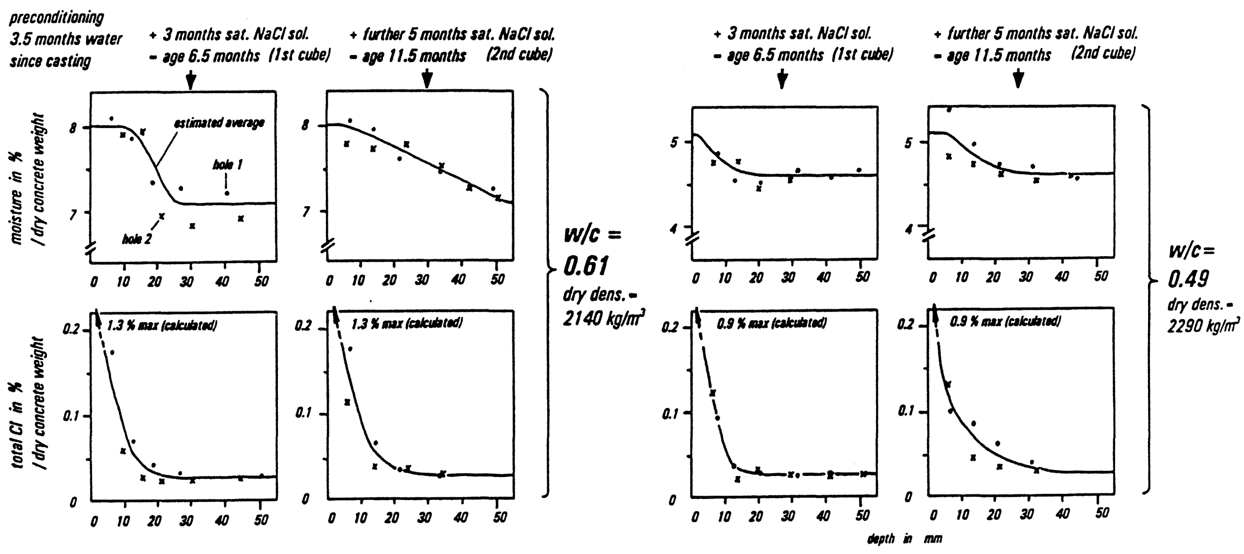


Fig. 92. The effect of hydration suction and filtering of sucked-in chlorides on water-, chloride-, and sodium profiles in concrete /102/.

The chloride concentrations measured in the filtered chloride profile may be considerably higher than the average concentration of sucked-in chlorides, depending on the filtering capacity of the binder. The filtering effect is schematically illustrated for sucked-in water, chlorides and sodium by Volkwein in Fig. 92 /102/.

As a consequence of hydration suction and the filtering effect, effective chloride "diffusivities" evaluated from chloride profiles at early ages would be initially very high, but decreasing over time. Therefore, the mechanism of hydration suction and filtering of sucked-in chlorides may contribute at least to some extent to the falling effective chloride "diffusivities" over time as observed also for submerged concrete.

11.7.4 A discussion of osmotic transport of chloride in concrete

As discussed by Larsson, Hedenblad and Claesson /104-106/ among others, reverse osmosis may cause significant chloride transport into concrete pores affected by a surface tension. The osmotic pressure created by a surface tension in not fully water saturated pores may be orders of magnitudes higher compared to the osmotic pressure created in a fully water saturated pore system.

Entrapped air may remain for very long times in a submerged concrete, since the process of diffusion of dissolved gases is very slow in concrete. Therefore, osmosis may have some practical significance also for submerged concrete, but the effect is probably larger in semi dry concrete affected by moisture gradients. Claesson and Hedenblad have theoretically calculated osmotic pressures of several atmospheres in semi dry concrete. /105,106/.

11.8 Field and laboratory studies of chloride binding in concrete, mortar and paste

11.8.1 General

Some more results and discussions on chloride binding in concrete, mortar and paste are presented, as a complement to the information given in Chapter 5 and in section 11.5.

The non-linearity of chloride binding was illustrated in Fig. 19 (C) using data presented by Sørensen and Maahn /72/ from a Danish concrete bridge exposed for 15 years in the marine upper splash zone. Similar chloride binding curves measured on cement paste under isothermal (20°C) laboratory conditions were shown in Fig. 19 (A) and (B).

11.8.2 Laboratory studies of the chloride binding

Several laboratory studies have indicated a strong concentration dependency for the chloride binding in hydrated cement paste and mortar /69-73,75/. As discussed by Pereira and Hegedus /107/, a general concentration dependency for the absorption of ions in porous material would be expected by analogy with the absorption processes relevant for chemical engineering.

Sergi and Page /75/ and Tang and Nilsson /70/ have later experimentally confirmed under isothermal conditions that the relationship between bound and free chlorides can be approximated by general adsorption isotherms. Tang and Nilsson /70/ indicated that the Langmuir adsorption isotherm is valid at free chloride concentrations < 0.05 mol/l, probably due to monomolecular adsorption of chloride ions. They found the Freundlich adsorption isotherm applicable at free chloride concentrations > 0.01 mol/l.

11.8.3 Studies of the field chloride binding in concrete exposed in the submerged and tidal zones

The evaluation of chloride binding data from concrete exposed in the submerged and tidal zones is complicated by the leaching of hydroxides as previously discussed. Since chloride binding increases with a decreasing hydroxide ion concentration /69,71/, chloride binding in hydroxide leached but not carbonated concrete will bind more chlorides than predicted by adsorption isotherms not taking the hydroxide concentration into account. The hydroxide effect on the adsorption isotherm was shown in Fig. 19.

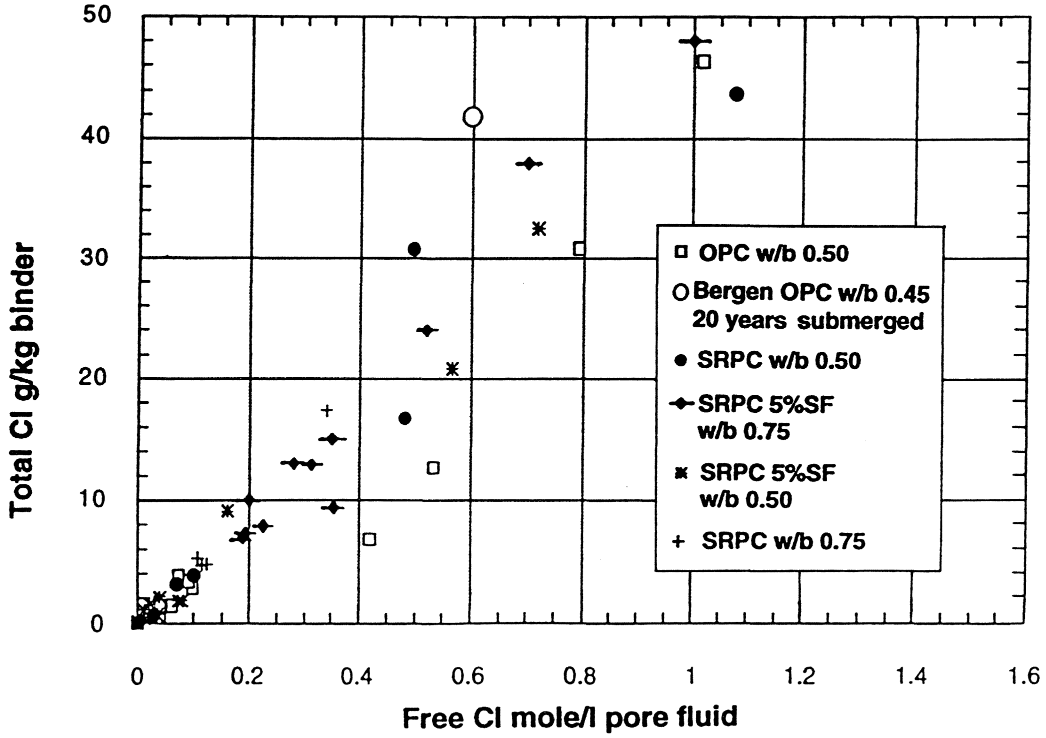


Fig. 93. The relationship between free and total chlorides measured by the pore solution expression method, in Portland cement concrete submerged for 7-14 months at the Träslövsläge marine field station /73/. Long term data (20 years) from submerged concrete at Bergen are indicated as well /109/.

The chloride adsorption relationships illustrated in Fig. 19 (A) and (B) reflect the adsorption at equilibrium in laboratory experiments. However, in most field studies and in the study by Sergi and Page /75/, a steep hydroxide gradient affects the relationship between bound and free chlorides.

As a consequence, the binder phase in the concrete bulk, at a high pH-value but with a low chloride concentration, will bind according to the lower curve in Fig. 19 (B). But the binder phase close to the concrete surface, not carbonated at a lower pH and with a high chloride concentration, will bind according to the upper curve in Fig. 19 (B). The net result may be a more straight relationship between bound and free chlorides, as reported by Tuutti /8/ and frequently found for submerged concrete exposed at Träslövsläge Field station, see Fig. 93.

The chloride binding data presented in Fig. 93 were measured by means of the pore solution expression method. The concrete specimens at Träslövsläge field station /73/ had been exposed for 7-14 months and were thus affected by a steep hydroxide gradient. As a long term reference, data from a 20 years submerged concrete at Bergen /109/ with almost no hydroxide gradient, was indicated as well in Fig. 93.

11.9 Measurements of the calcium and chloride enrichment in pore solution expressed from submerged concrete and cement paste

11.9.1 General

Chloride concentrations in expressed pore fluid from concrete submerged in sea water have occasionally been found to be higher as compared to the surrounding sea water /104,108,125/. Similar unexpectedly high concentrations in expressed pore fluid from submerged concrete have been observed regarding calcium ions /104,120,125/. Some results and a discussion of the phenomenon are presented.

11.9.2 Enrichment of calcium ions in the expressed pore solution

The ingress of chlorides into the pore solution in concrete apparently have a significant effect on the chemical equilibrium. Calcium ions in a chloride free pore solution from unleached concrete have a solubility much less than 0.01 M, as the calcium solubility is depressed by the alkali hydroxides in the pore solution /111/.

However, 1-2 orders of magnitude higher free calcium concentrations in chloride contaminated concrete have frequently been measured /120/, as illustrated in Fig. 94. Yonezawa attributed the apparent increased calcium solubility to the higher ionic strength in chloride contaminated concrete /120/, but the phenomenon has been observed also for chloride contaminated concrete at quite low ionic strengths /87,88,113,114,130/.

As reported by Theissing et al /130/, sodium chloride have a much less dramatic effect on the solubility of calcium hydroxide as compared to the concentrations indicated in Fig. 94. Theissing et al proposed the formation of a calcium hydroxide - calcium chloride hydrated complex in the presence of chlorides, thus affecting the chloride activity and also accounting for some calcium and chloride fixing.

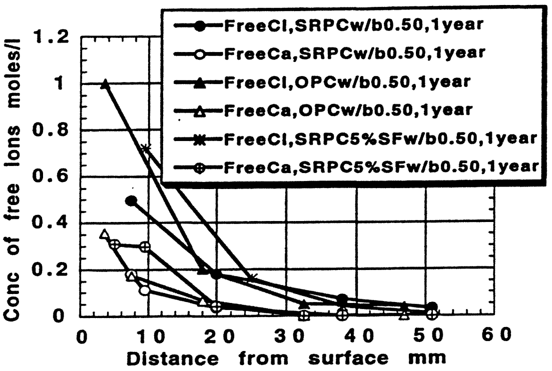


Fig. 94. Concentration profiles of free calcium and chloride ions measured by the pore solution expression method, in marine concrete of w/b 0.50, submerged for one year. The normal solubility of calcium is less than 0.1 M. The sea water had a chloride ion concentration of approximately 0.4 M/125/.

Moragues et al proposed that calcium and chloride form molecular dissolved species in the pore solution, thus altering the calcium activity in the pore solution. Such a molecular dissolved species would be mobile in the concrete pore solution, therefore being expressed from the concrete by the pore solution expression method. They proposed that the molecular dissolved calcium chloride species may dissociate when analyzed, by titration, etc., therefore explaining the high apparent concentration of free calcium ions in pore solutions containing chlorides /113-114/.

Chatterji on the other hand proposed that calcium ions co-diffuse, at very high concentrations, with chlorides, but the calcium ion transport would take place only in the electrical double layer /87-88/. However, since the electrolyte in the very thin electrical double layer is impossible to remove by the pore solution expression method, the high calcium concentrations found by this method apparently cannot be explained by the theory proposed by Chatterji.

11.9.3 Enrichment of chlorides in the expressed pore solution

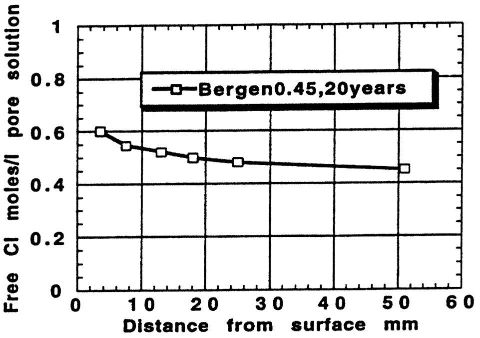
The phenomenon of chloride enrichment in expressed pore fluid from submerged concrete is illustrated in Fig. 94, for concrete samples of w/b 0.50 submerged for one year at the Träslövsläge marine field station at the Swedish west coast. The Träslövsläge sea water has a chloride ion concentration of approximately 0.4 M.

The chloride enrichment may be obvious for concrete exposed in the splash- and atmospheric zones, due to salt deposition and drying. However, for submerged concrete diffusion processes are commonly believed to eventually equalise the chloride concentration in the pore solution as compared to the external solution.

Indeed, long term immersion experiments of mortar and concrete submerged in the laboratory or in the field have indicated equalised or close to equalised chloride concentrations in the pore solution, at least if the w/b ratio of the concrete is less than 0.45 /104,109,120,131/.

In Fig. 95, the free chloride profile is shown as measured by the pore solution expression method, for a concrete of w/b 0.45, submerged for 20 years in sea water at Bergen. The hydroxide ion concentration was analysed as 0.039M, as was expected. Furthermore, no signs of calcium enrichment was found in the long term exposed concrete, as a free calcium concentration of 0.09 M was analysed. The sea water had an approximate chloride concentration of 0.55 M /109/.

Fig. 95. Concentration profile of free chloride ions measured by the pore solution expression method, in marine concrete of w/b 0.45, submerged for 20 yeas. The sea water had a chloride ion concentration of approximately 0.55 M /109/.



If it is assumed that the measured free chloride concentrations indicated in Figs. 94-95 are generally correct, they may support the belief that chloride transport in concrete is considerably affected by other mechanisms than that described by Fick´s 2 law of diffusion. Mechanisms such as suction + filtering, as proposed by Volkwein /102/, hydroxide leaching, osmotic pressure and other membrane effects /89,104/ may all affect the chloride transport in the concrete pore solution.

On the other hand, preliminary results on the effect of temperature on chloride binding by Larsson /104/, have indicated that the chloride binding may increase some 70-100% by lowering the temperature from +20 °C to +5 °C. Therefore it is possible that the "chloride enrichment" illustrated in Fig. 94 is related to the fact that the sampling was done at the field station at approx. +5 °C, but the pore solution expression was carried out a few days later at +20 °C.

Note that the mechanisms proposed by Moragues et al, the formation of molecular dissolved calcium chloride species, affecting the activity of calcium and chlorides, may also explain an apparent free chloride enrichment in the pore solution. However, their theory would not explain why the apparent chloride enrichment is strong at early ages, but diminishing when all concentration gradients are equalised at later ages.

Theissing et al /130/ proposed that the formation of a calcium chloride complex would explain the occasionally reported chloride binding properties of alite pastes. As discussed by Theissing et al, several conflicting results have been found regarding the chloride binding capacity of alite paste /130,132/. These conflicting results may further support the proposed existence of a calcium chloride complex, although such a complex may not be long term stable in concrete.

11.9.4 Reliability of the method of pore solution expression

As initially developed by Strelkov et al /123/, the pore solution expression method has generally been found to be the most accurate method for studying chlorides and hydroxides in the pore solution of concrete, mortar and paste /8,76,110,124/. Errors less than 10% have frequently been reported, provided that the amount of expressed solution is not too small, not carbonated and free of colloidal particles.

When discussing measurements on field samples being transported and stored for up to several days prior to the pore solution expression, errors much larger than 10 % must be assumed. However, repeated measurements of an enrichment of more than 100 % as illustrated in Fig. 94, are probably difficult to explain solely by the handling procedure for field sampling.

Several studies, /76,110,124/ among others, have indicated that the varying pressure applied will not significantly alter the composition of the expressed pore fluid. The pressures applied are in practice apparently too small to significantly alter the solubility of the chlorides and hydroxides, although the theoretical effect of some 100 MPa pressures on the solubility may be significant.

The composition of the expressed pore solution is likely to be very different from that of the solution in the electrical double layer, as discussed by Chatterji /87,88/. However, it can be argued that it is the composition of the, in this sense relatively large, capillary pores which has the major influence on the chloride transport in concrete and on the initiation of reinforcement corrosion.

A typical device for pore solution expression is shown in Fig. 96 /76/.

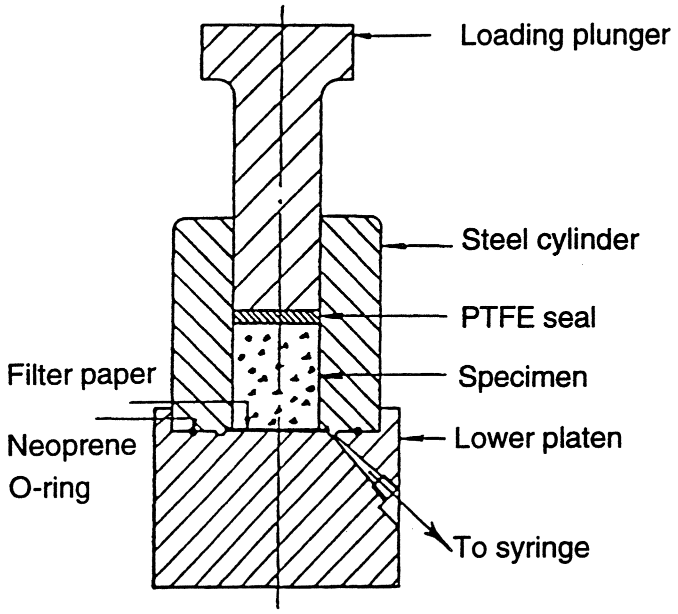


Fig. 96. Illustration of a typical device for pore solution expression /76/.

Since the enrichment found in laboratory exposure tests by Larsson in /104/ was observed for chlorides but not for hydroxides, and expressed pore solution was analysed simultaneously as the surrounding solution, errors in the analysing procedure are not probable as an explanation for the observations. If not considering the existence of molecular dissolved calcium chloride species, it is probably difficult to argue that the pore pressing procedure would affect extracted chlorides in a different way as compared to hydroxides.

Unfortunately, the pore solution expression method is usually not applicable for non-saturated concrete or very dense concrete. At present, no reliable method exists for analysis of the pore solution composition in modern high quality concrete of w/b ratios less than 0.45.

11.10 A discussion of the effect of hydroxide leaching on chloride transport in concrete at the first years of exposure

As reported by several researchers /75,110,120/, hydroxide ions sometimes have a higher diffusivity in concrete as compared to chlorides. As a consequence, hydroxide ions would be able to diffuse out from a submerged concrete more rapidly than chloride ions may diffuse into it. Since the charge balance must be maintained, however, the faster hydroxide ions would implement a driving force on negative ions transported in the other direction. Thus, the hydroxide leaching may accelerate the chloride transport rate as compared to normal diffusion.

Such a phenomenon may be regarded as a coupled effect of diffusion and electro-osmosis. The effect would decrease over time, as the alkali hydroxide content in the concrete is gradually removed.

Studies by Tang /90/, did not indicate any visible effect of the pH-value of the saline solution in alkalinity-controlled immersion tests, as compared to testing with no control of the pH-value. However, the pH-value was not continuously adjusted in the experiments by Tang.

On the other hand, the type of cation dissolved in a chloride solution is known to influence the result in a chloride permeability test. Therefore, the interaction of the cation with the binder appears to be relatively more important, although most surface densification phenomena depend on the alkalinity at the surface. As an example, calcium and magnesium ions co-diffusing with chloride ions would cause precipitation when in contact with the alkaline concrete, but highly soluble sodium ions would continue to diffuse.

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