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Fidjestöl, Per; Tuutti, Kyösti

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THE IMPORTANCE OF CHLORIDE DIFFUSION

Per Fidjestöl och Kyösti Tuutti

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The importance of chloride diffusion

Authors: Assoc. Prof. Per Fidjestöl, Agder College, Engineering Faculty[1] and Prof. Dr. Kyösti Tuutti, Lund Institute of Technology, Building Materials[2]

SUMMARY

In recent years a growing interest in the effect of chloride diffusion into concrete has resulted in a number of studies, both in the laboratory and in the field. Important and often expensive decisions regarding design or maintenance of structures are made based on such studies. Thus a thorough consideration of the methodologies used to obtain and to interpret the data is important. However, in the search for optimum chloride diffusion models, the main issue, structural lifetime, sometimes appears to have been lost.

In practice, the diffusion of chlorides into concrete will be important in one aspect only: when it causes initiation and growth of critical corrosion in such a way that the lifetime of the structure is severely impaired. Thus the importance of chloride diffusion through homogenous concrete must be considered in the light of the other factors of the corrosion process. The paper attempts to highlight some aspects that are valuable in a more total evaluation, such as the total corrosion process and its interaction with a lifetime model.

Introduction

There is growing trend to use models for predicting and estimating service life for concrete structures. Reinforcement corrosion is an important deterioration mechanism, and the model normally used to illustrate service life in this case is shown in figure 1. Here the lifetime is divided into an initiation and a propagation period.

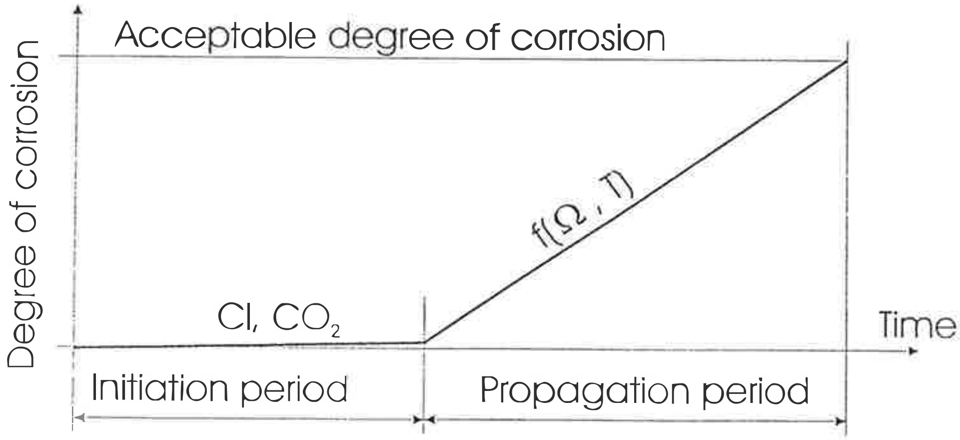

Figure 1. Schematic sketch of the corrosion process of steel in concrete.

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[1] Also with Elkem a/s Materials, Kristiansand, Norway

[2] Also with Skanska Teknik AB, Stockholm, Sweden

Understanding of the conditions that cause corrosion of reinforcing steel and prestressing steel is of vital importance. Avoidance of these conditions is necessary if concrete structures with steel are to have the intended longevity.

Since steel in concrete normally is protected against corrosion, the process of corrosion in concrete is divided into several phases, corresponding to the diagram above:

- Initiation - the negation of the protective mechanism
- Corrosion growth - the corrosion process is established and corrosion progresses
- Damage - The structure is sufficiently damaged that corrosion is considered severe.

In the paper, the impact of various factors on the modelling of lifetime is considered. Chloride diffusion is given ample space because of the amount of effort put into such studies, but questions are raised concerning the appropriateness of the single minded pursuit of the diffusion coefficient that one often feels prevalent.

Corrosion process

The high alkalinity (pH>12.5) of concrete normally protects embedded reinforcement in concrete from initiation of corrosion. When oxygen is present, the alkalinity of the pore solution causes an oxide film to form on the steel surface. This oxide film is has very low solubility, and thus the steel appears to be protected against corrosion. The steel is said to exhibit passive behaviour due to this oxide film.

The durability of the concrete in the cover maintains and protects the alkalinity and thus the passive film. If the passive film breaks, corrosion can begin. The film can break locally so that a few localised corrosion attacks result, or if breakdown occurs over larger areas, general corrosion takes place. Main causes of film breakdown include;

- Chemical, physical or mechanical breakdown of the concrete cover.
- Chloride penetration to the reinforcement.
- Carbonation of the concrete to reinforcement depth

Carbonation: The reaction between carbon dioxide from the air and alkalies in the concrete causes a reduction in the pH in the concrete to levels of 8 to 9, resulting in the loss of passivity. Corrosion follows, but the rate will depend on availability of oxygen and on the electrical resistivity of the concrete.

Local breakdown due to chlorides: (Pitting). Chlorides at a certain level of concentration will cause local breakdown of the passive layer, leading to very localised and therefore potentially very intense corrosion attack. The rate depends on the availability of oxygen, on the anode to cathode ratio and on the resistivity of the concrete. The concentration of chlorides necessary to cause breakdown of film will depend on the pH of the pore water, on the quality of the oxide film and on the properties of the steel/concrete interfacial layer.

Once corrosion has been initiated, the corrosion of steel in concrete is an electrochemical process with an anode where oxidation takes place and a cathode where reduction takes place. At the anode, electrons are liberated and ferrous ions are formed:

$Fe -> Fe^{++} + 2e^-$

at the cathode electrons are consumed and hydroxyl ions are liberated

$H_2O + ½O_2 + 2e^-\ \ 2(0H)^-$

The ferrous ions may subsequently combine with oxygen or hydroxyl ions and produce various forms of rust. This rust is what stains the concrete surface or causes cracking of the cover.

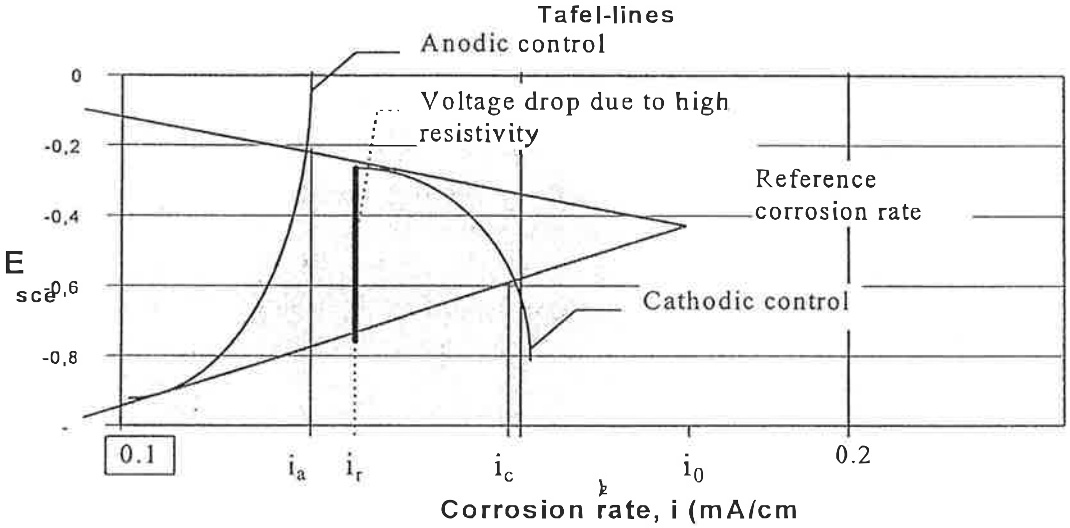

Figure 2 Tafel-lines obtained for mortar cast with 1.5% Cl⁻. The diagram shows reduced corrosion currents due to the possible limiting mechanisms mentioned below.

Regardless of the time to initiation, the rate at which the corrosion takes place will depend upon which process controls the corrosion rate:

> Anodic control; can often be understood as concentration polarisation at the anode. This means that corrosion products formed at the anode are not removed at a sufficient rate, or the corrosion products have low solubility and protect against further dissolution of metal such as by passivity. i_a
>
> Cathodic control; the reduction of oxygen at the cathode limits the corrosion rate. Can be caused by low availability of oxygen at the steel surface, e.g. in submerged concrete. i_c
>
> IR-control; the resistivity of the electrolyte, concrete, is so high as to limit the amount of current that can be developed from the two half-cell reactions, i_r. As an example, mineral additives can give very high electrical resistivity in concrete. A number of works available show that silica fume in particular, but also GGBS or fly ash will give concrete resistivities far in excess of what is provided by Portland

Cement concretes[9,10,11,12]. The high electrical resistivity of blended binder systems is confirmed by tests of "chloride diffusivity" using ASTM C1202 (also known as AASHTO T277) (the test determines resistivity as much as anything else, but has been found to relate acceptably to chloride diffusion found by more conventional diffusion or ponding tests)[13,14,15,16]

Modelling the initiation phase

Carbonation, which is a relatively well defined chemical process, can be treated with an acceptable precision in models. Theoretical calculations, when compared with practical experience, will have the same order of magnitude.

In marine or chloride rich environments, the major efforts made have been to analyse chloride profiles as a function of material parameters. Only a fraction of all activities have been spent on analysing the whole lifetime.

It is established that a certain chloride concentration in the pore water in concrete will cause corrosion. Chloride ions are able to penetrate concrete from the environment which is surrounding the structure. The availability different binders as ordinary Portland cement (OPC), mixed products containing OPC, slag, pulverised fly-ash (PFA) etc. have increased research activity into the durability of concrete. The main field of this research have been the comparison of diffusion coefficients and the binding capacity of chlorides in the cement matrix, but unfortunately it is not sufficient to simply determine the chloride penetration because such values do not indicate the service life of the structure. It is also necessary to know the chloride content at the initiation moment ince this will be the threshold value.

Theoretical calculations and models of the time of initiation in a chloride rich environment often demonstrate the lack of knowledge for the important parameter, the threshold value of chloride ion concentration. A demonstration of this can be seen in figure 2. Normally one would assume that the sample with the lowest chloride concentration is preferable. Figure 2 demonstrates that the situation can be the opposite.

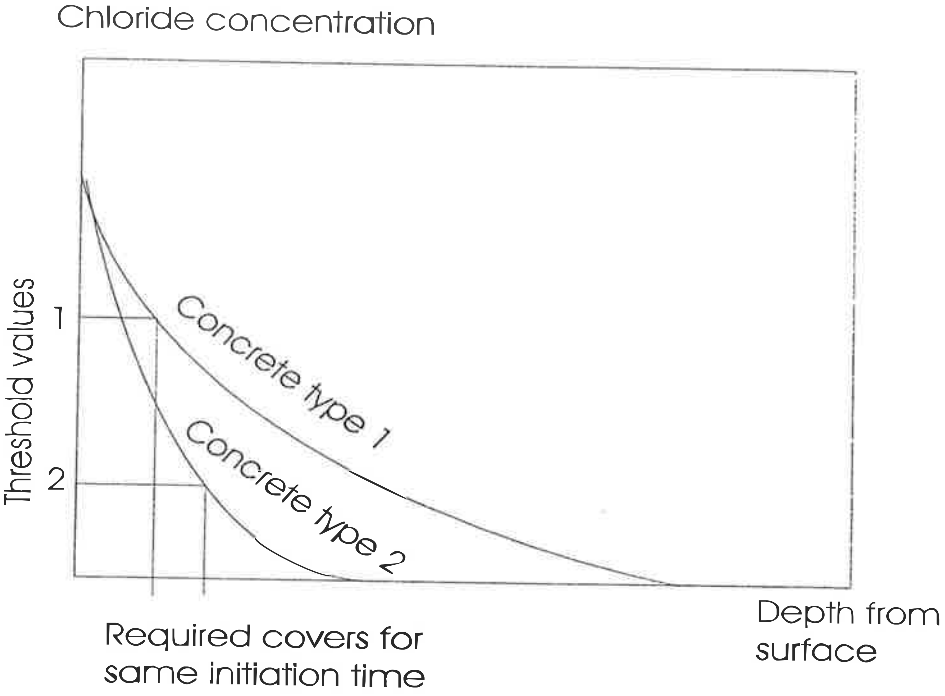

Figure 3. Schematic sketch of initiation depth for two different concretes.

Chloride threshold values

The chloride threshold level depends on so many parameters thatfirm statements are difficult to make. Many investigations report critical chloride concentrations with a lowest value of around 0.2 - 0.4 % by weight of cement. Also several national codes use those low values as the allowable amount of chloride in concrete. On the other hand many investigations indicate much higher threshold values around 1 - 2 % by weight of cement, Lambert, Page and Vassie [5], Pettersson [6], Pettersson and Woltze [7].

Between 1950 and 1960 numerous results were obtained using calcium chloride admixtures as the accelerator. Laboratory and practical experiments showed an expected threshold value of 2 - 3% by the weight of cement. These samples were both small and large, with a very homogeneous concrete surrounding the reinforcement; the climate was in other words constant.

If such experiments were made under other climate conditions, however, drying and wetting procedures would have increased the chloride concentration close to the steel surface in an inhomogeneous way, an effect which certainly would have changed the reported results. In the same manner thick concrete covers will increase the homogeneity around the embedded steel.

This difference indicates the problems involved. The most important factor which will give such variable results as above, is the transport or the exchange of water, oxygen, corrosion inhibiting ions and corrosive ions. Therefore such variations must be taken into account in all comparison tests and life time predictions.

Chloride concentrations in the surrounding environment could be high or low. An increase of the chloride concentration in the environment will give the same effect as a reduction of the threshold value. All chloride concentration profiles are related to the concentration at the surface. The threshold value is on the other hand relatively constant, which will reduce the relative value of the threshold compared to the surface concentration when this is increased.

Recent results by Pettersson and Woltze [7] show that different binder combinations will have different threshold values. The moisture condition will also influence and complicate the prediction of threshold values in structures in service. However, structures have to be designed in such a way that the concrete quality combined with the effect of the concrete cover will cause a minimum of moisture variations close to the steel surface. If these design rules is used, it may eventually make it possible to predict the service life of a concrete structure.

Threshold values could be determined with the help of advanced electrochemical methods that can detect the onset of corrosion, see Andrade /8/, Lambert /5/, Pettersson /6/. After initiation the pore water close to the steel surface must be analysed which will give the threshold value. It should be pointed out that it is important to measure the free chloride concentration in the pore water in this stage. It is also important to do these measurements with an adequate concrete cover. Small concrete covers will give underestimated results because the transport of other elements in the system will give a strong influence on the threshold value (eg. leaching of $(OH)^-$).

The creation of a rapidly growing pit also depends on the availability of a cathode. Thus, even if the threshold value may be exceeded including at crack tips, the steel may repassivate if the necessary cathode capacity is not available. Since most available knowledge hails from tests on steel in alkaline solutions or of steel in "conventional" concretes, the question arises whether so-called high performance concretes with high resistivities in the cover, will lend themselves to the same kind of pit growth as is traditionally assumed.

Pitfalls in traditional studies

Cracks

In research studies onee likes to analyse homogenous samples in order to simplify the complex corrosion process. However, chloride ions will penetrate and reach the steel in cracked areas extremely fast. One year will be overestimates the time here. Is that short period the end of the service life? Certainly not with regard to practical experience. The electrochemical reactions will be influenced by the small size of the areas where corrosion can take place. A high concrete quality, with a high resistivity, could not create large cathodic areas and a correspondingly high corrosion rate. Thus threshold values could be of another magnitude in a cracked microzone.

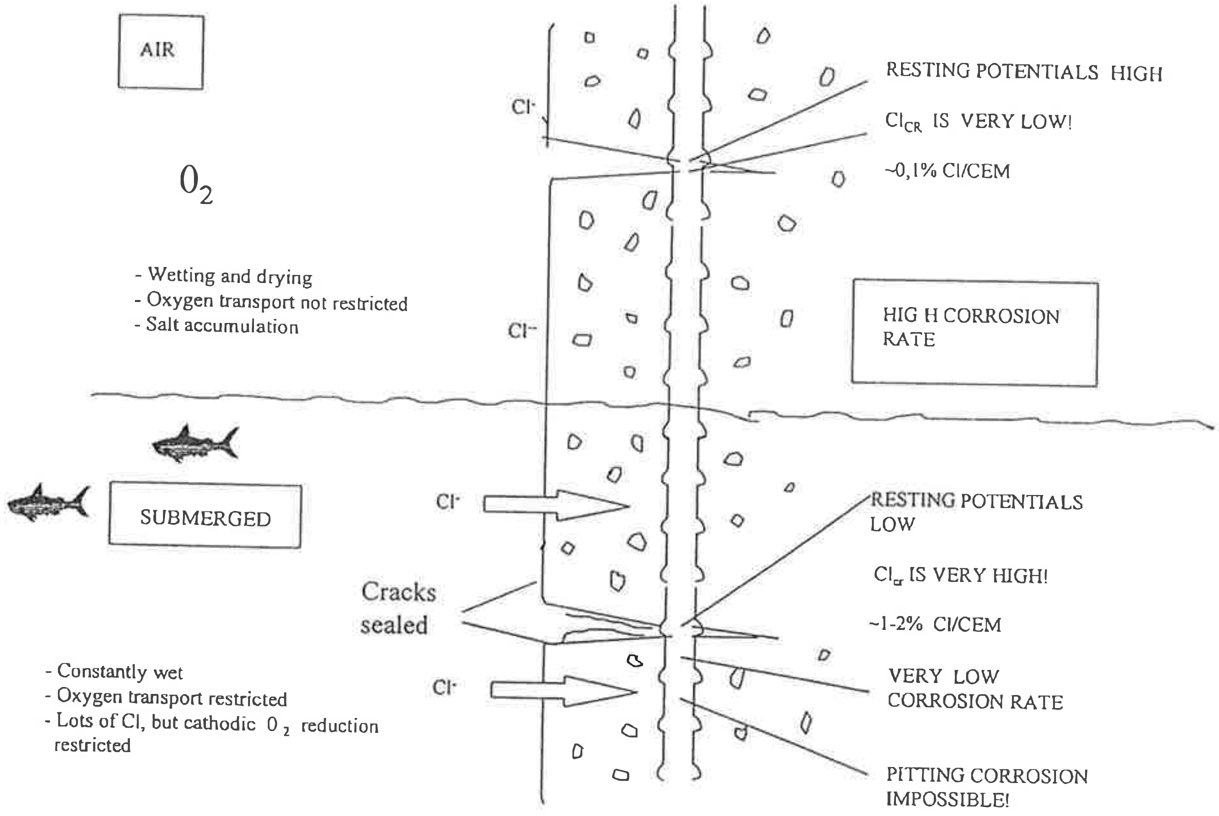

Figure 4. A schematic sketch of the effect of a marine environment on concrete. Sandberg 1995, personal communication.

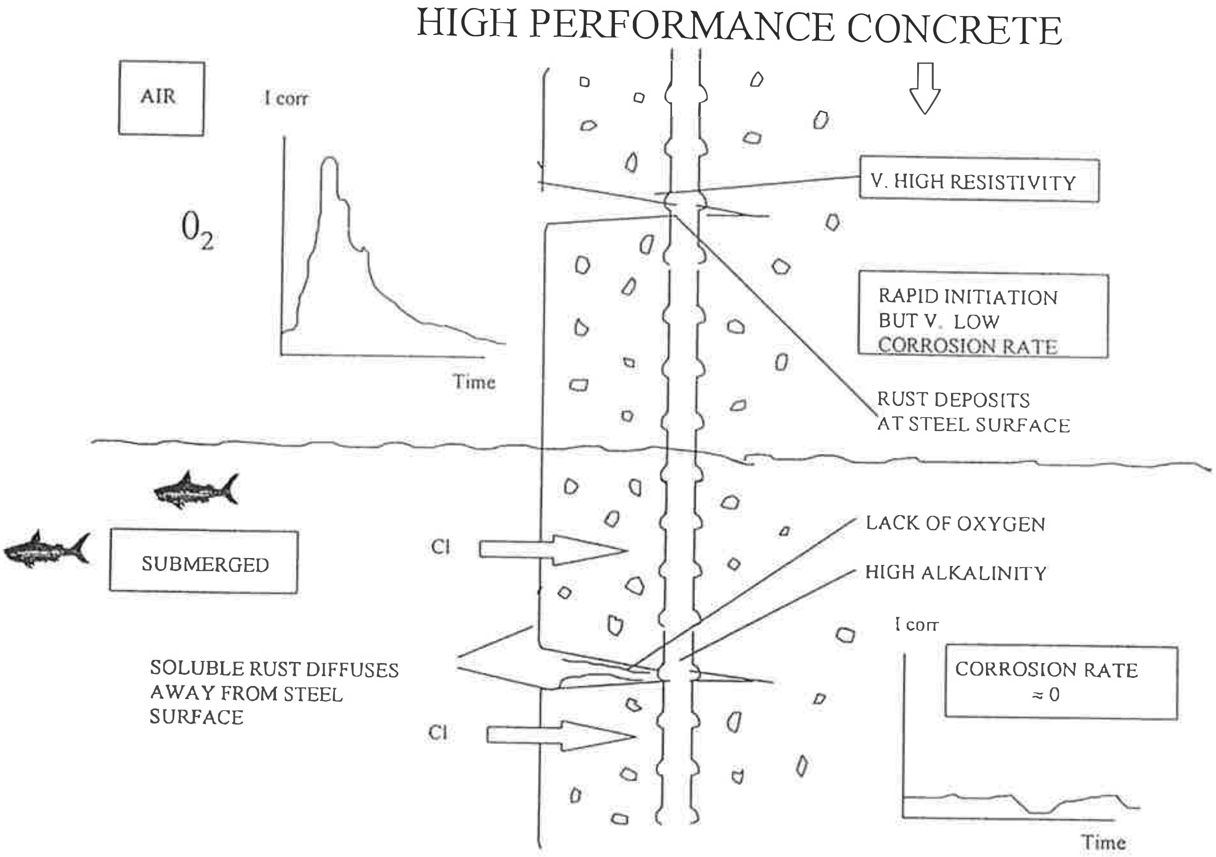

Figure 5. Effect of high performance concrete on corrosion process. Sandberg 1995, personal communication.

The importance of imperfections

An old Finnish colleague, Prof. Sneck, mentioned 20 years ago laboratory tests he was carried out. Rebars were first treated in a cement paste with a water/cement-ratio of about 0.40. Thereafter the rebars were cast into different concrete qualities with an initial amount of mixed-in chloride. The interesting finding was that Prof. Sneck could not create a corrosion process, even when the chloride concentration was about 5% by weight of cement. This simple test indicates that corrosion of steel in concrete could only be initiated in cavities or improper concrete around a steel surface.

Fidjestöl exposed with cracked concrete specimens on the seabed outside Bergen 20 years ago. Almost immediately the cracks in the concrete were found to be sealed by magnesium and calsium salts, and no corrosion were detected at all. This year, 1995, these old samples were once again examined without any sign of visual corrosion attack, despite chloride concentrations at the level of the steel far higher than that of the sea-water.

Microclimates

Norwegian studies of concrete bridges have also found that a bridge could contain many different environmental conditions as

- completely water saturated concrete

- concrete in the splash zone in the main wind direction
- concrete in the splash zone sheltered from the rain and wind
- concrete above the splash zone sheltered or not sheltered from rain and wind etc.

Therefore we could also expect that identical geometrical structures with different concrete qualities will behave completely different in

- moisture content
- results from electrochemical potential mapping
- threshold value
- corrosion rate
- critical crack width, etc.

even when comparison is made in same sections.

Questions as:

- which period will have the main effect on service life?
- does it matter with a short initiation period?
- could we expect concrete as a homogenous material?
- are cracks initiating the process of corrosion?

will give ideas of future research areas.

What determines lifetime?

The consideration of lifetime versus reinforcement corrosion has a strong philosophical aspect. The critical point in time can be considered to be any one of the four following:

1. Initiation of corrosion
2. Corrosion products become visible on the concrete surface
3. Cracking and/or spalling due to corrosion occur
4. The bearing capacity of the structure is seriously reduced due to loss of steel section

Traditional lifetime considerations consider only the initiation of corrosion, however, even for very visible structures, it could and should be considered to use criterion 2 or even 3 as the criterion and target for rational design.

Looking at it critically, the initiation of first corrosion in a structure will often be very rapid, due to defects in the cover. From then on, the critical factor is the corrosion rate. In modern infrastructure projects, a lifetime of 100 years or more is often desired, and in this context, it may be excessively optimistic to hope for a cover design that will prevent critical ingress of chlorides over this period.

Therefore, there is an important need to redefine what we mean by the lifetime of the structure, or at least formulate alternative definitions, suited to the occasion. Since, in essence, pieces of cover can in many cases fall off without the structure itself becoming threatened, other issues than structural safety are likely to be important:

- Aesthetics: Rust stains on the surface of high visibility structures are often undesired.

- Public opinion: Regardless of technical questions, people do not like to drive over bridges that have cracks in them often with rust showing through.
- Safety: Falling pieces of concrete are hard and can damage people and property.

In the light of such considerations, it is clear that the initiation phase is only a short part of the whole. In order to properly model the lifetime of a structure, much more attention must be paid to the consideration of the growth period. And, in order to provide adequate durability by economical means, the technological tools available for influencing the corrosion rate should be utilised fully.

TO CONCLUDE:

Corrosion is likely to be first initiated in cracks and other defects of the concrete cover.

Even with reasonably intact cover, the time of corrosion initiation can be expected to be well short of the desired lifetime for modern structures.

Therefore, the study of the actual corrosion process, and the rate-limiting parameters is required urgently.

In light of improved concrete technology studies are required on:

- pit formation in high-resistivity concretes,
- revision of existing crack-width criteria.

We must take a critical look at current research activity and ask if some of the effort, in the interest of long-life structures, should be directed from chloride diffusion studies to the other parts of the process.

Environmental effects are of great importance, especially the micro environment close to the steel surface. Since simple chloride profiles will not give any information of the state of the corrosion process, the simplified procedures of codes or tests are not necessarily relevant to the corrosion processes which will occur in practice. Better analyses which will take the micro climate inside the concrete into account are required.

Cracked concrete, with sealing effects from rust and diffusion processes in the microzone close to cavities around the crack, need more research before critical crack widths in different environments could be defined, especially for modern concretes.

Questions as:

- which period will have the main effect on service life?
- does it matter with a short initiation period?
- could we expect concrete as a homogenous material?
- are cracks initiating the process of corrosion?

also indicate future research areas.

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