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1995

Citation for published version (APA):
Fagerlund, G. (1995). *On chloride induced reinforcement corrosion in marine concrete*. (Report TVBM; Vol. 3061). Division of Building Materials, LTH, Lund University.

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1

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ON CHLORIDE INDUCED REINFORCEMENT CORROSION IN MARINE CONCRETE

Göran Fagerlund

Report TVBM-3061
Lund 1995

CODEN: LUDTVDG/(TVBM-3061)/1-18/1995
ISSN 0348-7911

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Lund, november 1995

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Summary

Reinforcement corrosion, initiated by the penetration of chloride ions from the surrounding marine environment, has for a long time been regarded one of the most difficult damage type to handle. On the basis of accelerated, or non-accelerated, chloride diffusion tests in the laboratory, diffusion coefficients have previously been derived, that indicate that extraordinarily dense concrete, and very thick concrete cover are required, if the service life before onset of reinforcement corrosion shall exceed 100 years, or more. New information, based on extensive field studies in Norway and Sweden, and supported by field tests from Denmark, indicates quite unambigously, that the diffusion coefficient of chloride in the real environment normally is considerably lower than in the laboratory. It seems as if a reduction in "the laboratory diffusion coefficient" by a factor of 10, or more, can be expected to take place in the real marine environment. This means, that a service life of 100 years might be achived by a high quality concrete with reasonably thick cover. Concretes with extremely low water/binder ratios are not required.

There is also other information, obtained during the last years concerning initiation of reinforcement corrosion. Part of this new information is accounted for in this report. The significance for the service life is briefly discussed. Much of the information is obtained from the National Swedish project "Marine Concrete Construction", which is sponsored by Cementa AB, and led by Professor Kyösti Tuutti and Lic Techn. Paul Sandberg. A comprehensive presentation, and discussion of data, from the National research project is made in Mr. Sandbergs licentiate thesis /17/.

1. Introduction

Chloride penetration has normally been treated in the following simplified way:

* A diffusion coefficient has been determined by some sort of accelerated test in the laboratory. This has been done by comparing the measured profile of total chloride with the theoretical solution to Fick´s 2nd law of diffusion, assuming constant conditions.

* The service life has been estimated, the concrete mix has been selected, and the concrete cover has been chosen on basis of the diffusivity measured in in the laboratory, and on a standard value of the total chloride concentration, that is required for the onset of corrosion.

Field tests performed during the last years in many places, and to a large extent in Scandinavia, has demonstrated that this procedure is far from correct:

* In reality, it is the *free* chlorides that are of interest in conjunction with corrosion, and not the total.

* In reality, the free chloride required for onset of corrosion is not a constant, but depends on the type of cement, on the type and amount of mineral admixtures, and on the water/cement ratio. It may also be a function of the exposure time, which determines the amount of dissolution of alkalies.

* In reality, the diffusion coefficient is often much lower than the laboratory diffusion coefficient. The relation between the two coefficients is bigger, the older the structure, and it is also different for different types of cement.

* In reality, there is not a constant relation between free and bound chloride. Therefore, the normal solution to Fick´s 2nd law is not applicable.

* In reality, there is probably another relation between free and bound chloride, than that obtained in an accelerated chloride diffusion test.

* In reality, the driving chloride concentration is often much higher than assumed when using the traditional calculation method. The free chloride at the surface might be considearbly higher than in the surrounding medium.

* In reality, there is chemical interaction between the concrete, and the surrounding medium; e.g. sea water. This is not the case in a laboratory test.

* In reality, there is ageing phenomena occurring in the surface of the concrete, due to varying temperature, frost etc.

2. Essential factors for service life

The service life before corrosion starts is mainly determined by four factors.

1: The threshold chloride concentration for start of corrosion.
2: The effective diffusivity of chloride in the concrete cover considering all phenomenons that might occur such as:
  - chemical reactions between the concrete and the environment, such as sea water
  - non-linear binding of chlorides; the shape of the binding isotherm
  - the water content in the cover; e.g drying caused by self-desiccation
3: The surface concentration of free chloride
4: The thickness of the concrete cover

3. The threshold concentration of free chlorides

3.1 No leaching of alkalies

The threshold concentration of *free* chlorides depends on the concentration of hydroxyl ions. The following very pessimistic, so-called Hausmann criterion, can be used; see Fig 1 /1/:

$$[Cl^-]_{thr}/[OH^-]=0{,}6 \qquad (1)$$

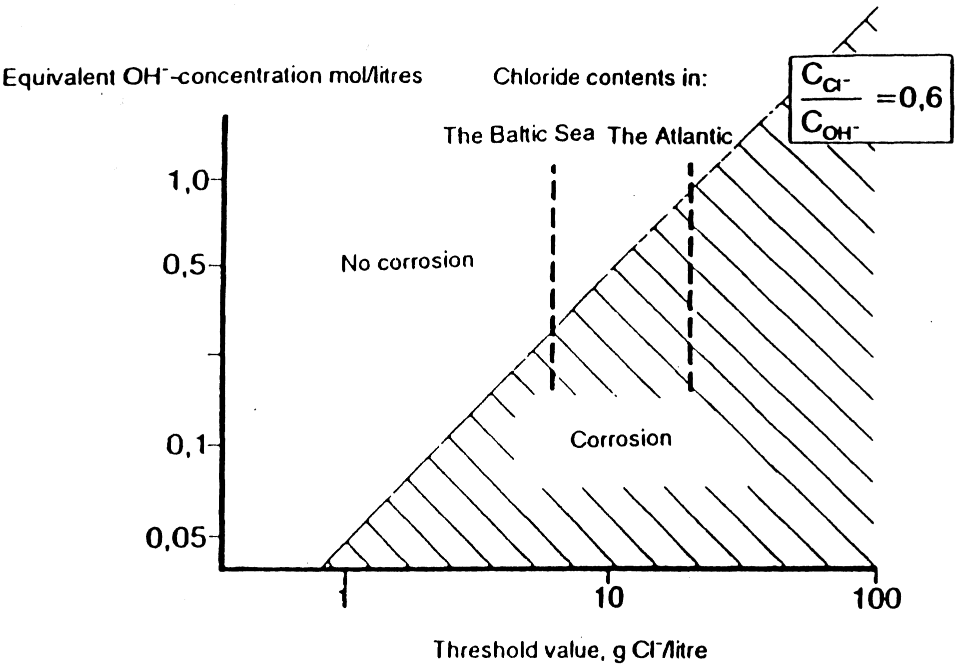


Fig 1: Relation between the OH⁻-concentration and the required free chloride concentration for start of corrosion of steel; /1/ as represented in /15/.

For a saturated concrete made with pure Portland cement, and with no leakage of alkalies, the hydroxyl ion concentration at the depth of the reinforcement is a function of the water/cement ratio, and a function of the alkalinity of the cement (no leaching of alkalies is assumed to occur on the depth where the reinforcement is located)[1] :

$$[OH^-]=C(Na/23+K/39)/P_{tot} \qquad (2)$$

Where		
	C	the cement content (kg/m^3)
	Na and K	the amount of Na and K as weight-*fraction* of the cement
	P_{tot}	the total porosity (m^3/m^3)

---

[1] In Eq (2) it is assumed that water in all pores, also in the gel pores, are able to dissolve chloride to the same extent. If only the capillary pores dissolve chloride, P in Eq (2) shall be exchanged for P_{cap} which is defined: $P_{cap}=C(w/c-0{,}39\cdot\alpha)/1000$ (with the same notation as in Eq (3).) This will increase the chloride concentration. Example: w/c=0,40, α=0,75: $[Cl^-]_{Ptot}/[Cl^-]_{Pcap}=0{,}42$

The total porosity is:

$$P_{tot}=C(w/c-0{,}19\cdot\alpha)/1000 \qquad (3)$$

Where α the degree of hydration
w/c the water/cement ratio

As an example, the formulas above will be applied to concrete made with a cement of the following chemical composition: K^+=0,005 kg/kg and Na^+=0,003 kg/kg This means that the equvalent alkali content is: $(NaO_2)_{eq}$≈0,8%.

Then, the OH-concentrations and threshold concentrations shown in Table 1 are valid for different concrete qualities. The degree of hydration is assumed to be 80% in all concretes.

Table 1: Example of calculated OH-concentrations and threshold concentrations

w/c-ratio	Cement content (kg/m^3)	Porosity (m^3/m^3)	[OH$^-$] (eq. mole/l)	[Cl$^-$]$_{thr}$ (mole/l)	(mg/l)
0,60	300	0,134	0,58	0,35	12250
0,50	350	0,122	0,74	0,44	15400
0,40	420	0,104	1,04	0,62	21700

Thus, the lower the w/c-ratio, the higher the threshold concentration. This has also been observed in practice; see Fig 2, /2/. The threshold values in this figure are, however, considerably higher than the theoretical; especially for low w/c-ratios. The theoretical value is, therefore, on the safe side.

The use of pozzolanic materials reduces the OH-concentration. One example is seen in Fig 3, where the effect of silica fume is shown; /3/. The reduction is marginal when the amount of silica fume is small, but it is very big at large dosages. The fact, that the addition of silica fume reduces the threshold concentration, is also seen in Fig 2.

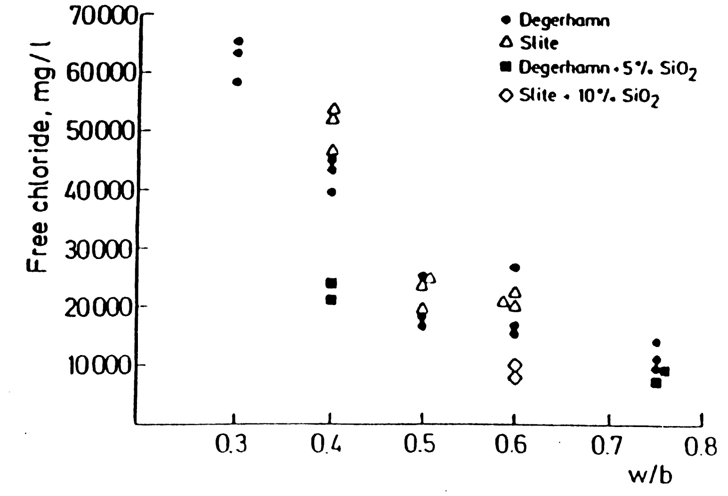


Fig 2: The threshold concentration of free chloride required for start of corrosion in cast-in reinforcement bars; /2/. Different water/binder ratios (w/b), two types of portland cement, 0%, 5% or 10% silica fume. The chemical characteristics of the cements are: *Degerhamn*: C_3A≈2%, (Na_2O_{eq})=0,5%. *Slite*: C_3A=8%, (Na_2O_{eq})=1,1%.

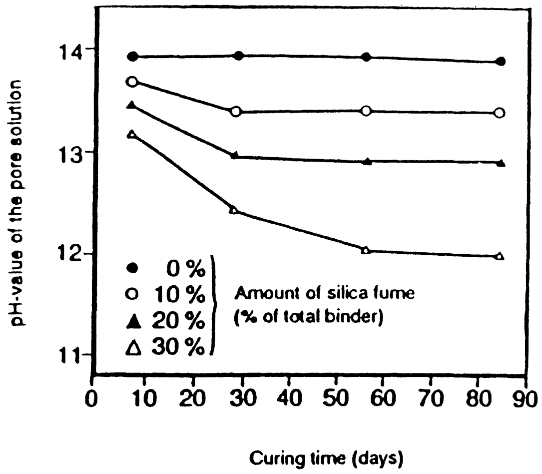


Fig 3: Effect of silica fume addition on the pH-value of the pore solution; /3/.

3.2 Effect of leaching of alkalies

One cannot exclude, that alkalies are gradually leached out of moist concrete. However, even if there is total leaching of all Na^+ and K^+, there is still a buffer of calcium hydroxide maintaining the pH-value of the concrete at a high level. One example is shown in Fig 3. It shows the pH-profile in the surface part of a 36 years old quay in Esbjerg in Denmark. The depth is calculated from the present surface of the structure. There has been a certain frost erosion, so that the real depth is some centimeters bigger than that measured. It is interesting to notice, that the pH-value almost completely corresponds to that of saturated $Ca(OH)_2$-solution. In the tidal zone, there is, however, signs of total leakage of calcium hydroxide to a depth of about 20 mm.

The real calcium hydroxide profile, and the soluble ion-profiles taken from the tidal zone of the same quay, are presented in Fig 4; /17/. The calcium hydroxide is reduced gradually from the surface, but is normal at a depth of 30 mm from the surface. The alkalies are partly dissolved on a still larger depth.

The water/cement ratio of the concrete in Fig 4 and 5 is 0,55. The leaching is, of course, lower for a concrete with the water/cement ratio of 0,40, or less. One is on the safe side, if one assumes that the pH-value at the level of the reinforcement bars is 12,5, corresponding to saturated calcium hydroxide solution. This gives the following OH^--concentration and threshold chloride concentration, assuming the Hausmann criterion, Eq(1), is valid:

$[OH^-] = 0,032$ mole/litre

$[Cl^-]_{thr} = 0,019$ mole/litre or 665 mg/litre

This threshold concentration is low, and very much on the safe side, for a concrete with as low water/cement ratio as 0,40, and a concrete cover as big as 75 mm. It is doubtful if total leaching of all alkalies will actually occur in a cover of this high quality. Probably, there will be a diffusion of alkali from the interior of the concrete, that replaces the alkalies leached out, and maintaining the high pH-value.

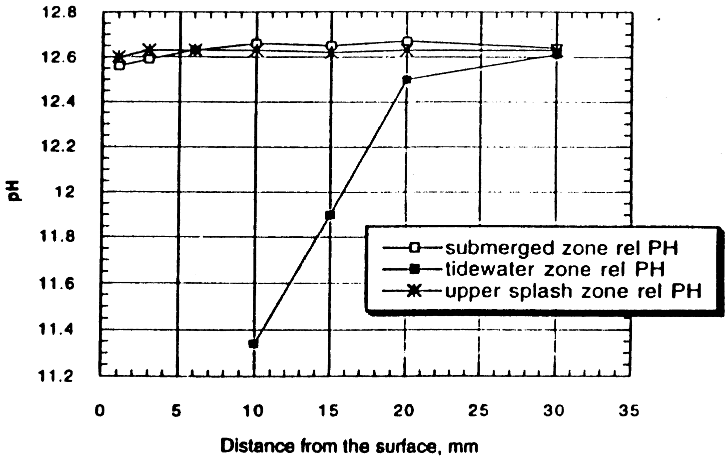


Fig 4: pH-profile in the surface part of a quay in Denmark, that has been exposed for 36 years to Sea water in the North Sea; /10/. (w/c-ratio 0,55)

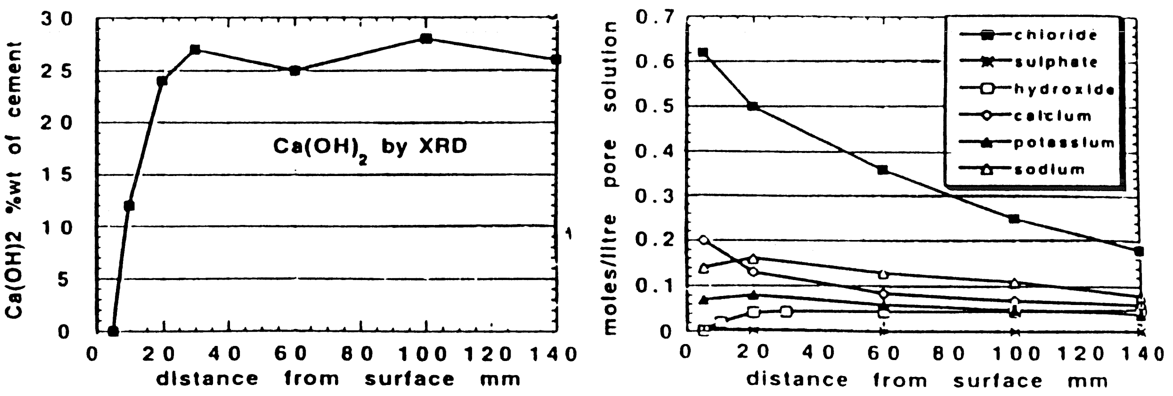


Fig 5: Calcium hydroxide profile and profiles of soluble ions in the surface part of the quay in Fig 4; /17/.

4. The effective chloride diffusivity

As said above, the effective chloride diffusivity is a function of many factors. One major factor is the binding capacity. Normally, one assumes that the binding is linear; i.e. the amount of bound chloride is proportional to the total amount of chloride. Then, the diffusion can be calculated by the common solution to Fick's 2nd law, assuming that the diffusion is determined by an effective and constant diffusion coefficient, which is a function of the assumed constant ratio between free and bound chlorides.

In reality, the binding isotherm seems to be highly non-linear. Two examples are seen in Fig 6 and 7; /4/ and /5/. Fig 6 shows that the binding isotherm is extremely non-linear; much more chloride is bound at low chloride concentrations, than at high. Fig 7 shows that the isotherm is also a function of the OH-concentration; therefore, considerably less chloride is bound in a concrete containing silica fume.

Nilsson /6/ has shown, that a non-linear binding isotherm leads to a totally different solution to the diffusion equation. The chloride profile becomes markedly S-shaped. If this is not considered, an extrapolation of the future chloride penetration from a short term penetration profile will lead to big a under-estimation of the residual service life.

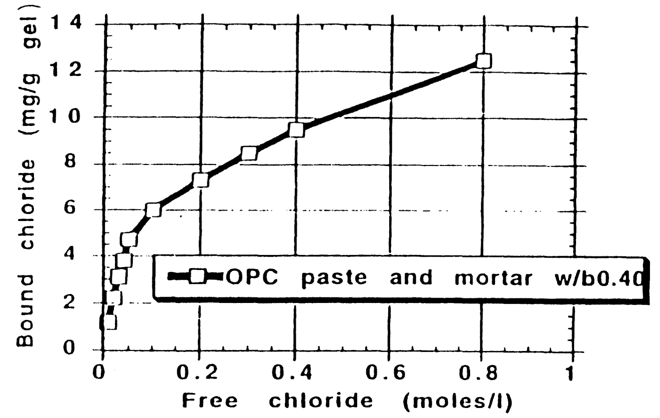


Fig 6: The relation between free and bound chloride; /4/. Water/binder ratio 0,40.

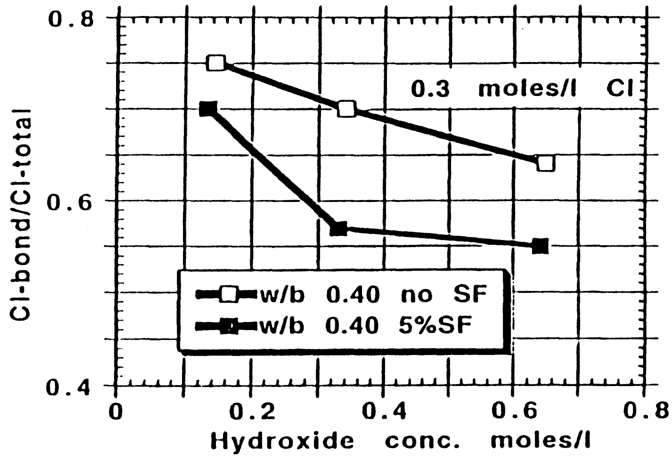


Fig 7: The relation between the ratio bound and total chloride and the hydroxide concentration of the pore water; /5/. Total chloride concentration 0,3 mole/litres. (SF=silica fume)

The effective chloride diffusivity is reduced very much during field exposure to the marine environment. Two examples are shown in Fig 8 and 9. The concretes in Fig 8 were exposed in the North Sea for periods between a couple of months and 30 years; /7/. Specimens were taken from the surface part of the structures. The chloride profile was determined at the exposed surface. From this, an effective diffusivity, D_{eff}, can be calculated. The unexposed part of the specimens, not being chloride infected, was subjected to an accelerated diffusion test. After 35 days, the chloride profile was investigated. From this, a so-called bulk diffusivity was calculated; $D_{bulk\ diffusion}$.

The relation between the real effective diffusivity, and the bulk diffusivity, is shown in Fig 8. The real diffusivity is much lower and the difference between the two values increases with increasing concrete age. A reduction by a factor of about 20 is obtained after 20 years.

Similar observations were made in Sweden for concrete, that was exposed to water in the Baltic Sea. The concrete investigated was taken from the concrete in a repair of the Öland bridge. The reduction in the diffusivity is of the same order of size as in the Norwegian study; see Fig 9, /8/. The curve is the effective diffusivity determined from the chloride profile of the exposed concrete. The points are the diffusivities determined in the laboratory on a non-chloride infected part of the concrete after 180 and 1387 days of exposure, and on a sample of the virgin concrete after 35 days. The test method used is described in /9/.The reduction in diffusivity is very big. It starts with $8 \cdot 10^{-12}$ m^2/s for the young concrete, and it falls to $0,3 \cdot 10^{-12}$ m^2/s after 1387 days in sea water; a reduction by a factor 27.

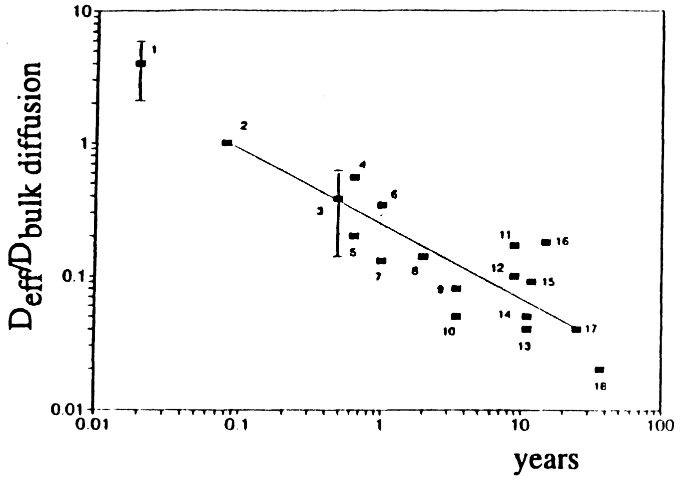


Fig 8: The effective chloride diffusivity in concrete exposed to sea water for long time, versus the diffusivity determined in the laboratory on the virgin concrete. Many concretes with different mix proportions; /7/.

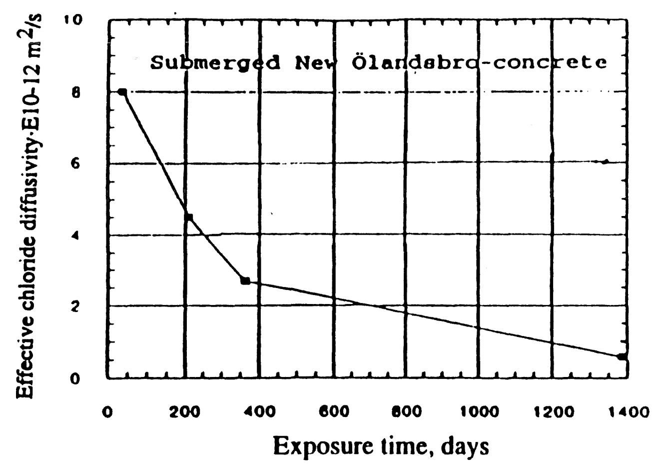


Fig 9: The effective chloride diffusivity in a concrete taken from the repair of the Öland bridge, and exposed to water during 1400 days, versus the diffusivity determined in the laboratory on the virgin concrete; /8/. Pure portland cement with $C_3A \approx 2\%$, $(Na_2O_{eq}) = 0{,}5\%$. w/c=0,40.

The reduction seems to be depending on the type of concrete. One example is shown in Fig 10; /10/. The three concretes have been exposed at the field station in Träslövsläge in Sweden. The first value for each concrete is the bulk diffusivity determined in the laboratory by the method described in /9/. The other two values are the effective diffusivities determined from the measured chloride profiles of the exposed concrete. The reduction in the diffusivity during a period of 14 months in sea water is very big in the concrete with pure portland cement, small in the concrete with 5% silica fume, and none (or a slight increase) in the concrete with both silica fume and fly ash.

The reason behind this reduction of the effective diffusivity is unknown. Possible explanations are:

* Chemical reaction with the sea water makes the concrete surface more dense. The reaction is smaller when the concrete contains mineral admixtures. Alternatively, concrete with mineral admixtures obtains some micro-cracking, which are reducing, or eliminating, the densifying effect of the chemical reaction.

- * Continuous hydration making the concrete more dense. It might be that a pure PC-concrete hydrates during a longer time, than does a concrete containing mineral admixtures.
- * A time-dependent chloride binding; i.e. the binding isotherm is time-dependent. It might be that this effect is bigger in a PC-concrete.

None of these hypotheses has been confirmed.

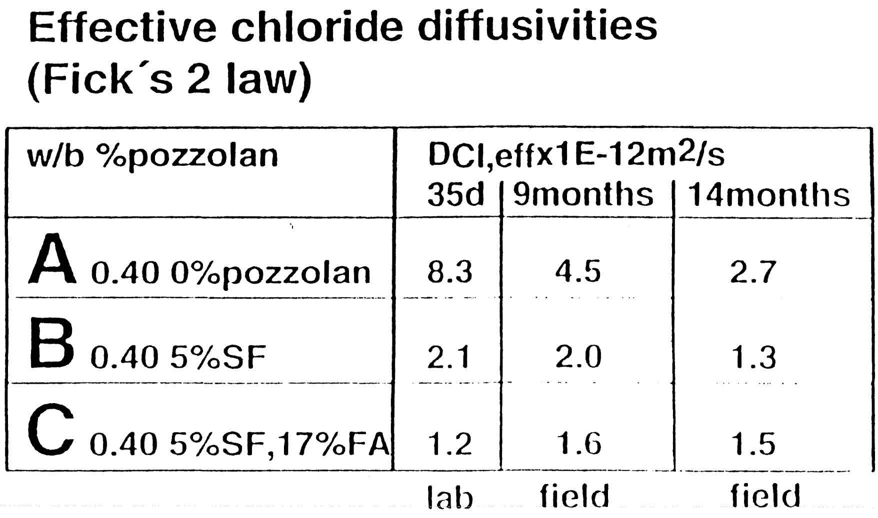
According to the solution to Fick's 2nd law, the penetration of a certain constant chloride concentration, e.g. the critical concentration, proceeds according to a square-root-of-time relation. This is not the case with a diffusion coefficient, that is gradually reduced. Instead, the penetration of a fixed level of concentration can approximately be described by the following type of relation:

$$z_c = \text{const} \cdot t^{\beta} \qquad (4)$$

Where

z_c	the distance from the surface to the chloride front where the concentration is c
t	the exposure time
β	an exponent, that is smaller than 0,5 and which might also be zero or even negative. β is a function of time

When β is zero, the penetration front stops moving inwards. This type of behaviour has also been observed in practice. Two examples are shown in Fig 11 and 12; /10/. The concrete in Fig 11 is a PC-concrete with low-alkali/low-C_3A cement with the water/cement ratio 0,40. The penetration continues between 210 days and 363 days, but with reduced diffusivity; from $4{,}5 \cdot 10^{-12}$ m^2/s to $2{,}7 \cdot 10^{-12}$ m^2/s. The concrete in Fig 12 is made with the same cement, but 5% dry silica fume has been added. The water/binder ratio is kept constant. Now the penetration front is almost constant with the exposure time. The chloride diffusivity is reduced from $3{,}4 \cdot 10^{-12}$ m^2/s after 285 days, to $1{,}3 \cdot 10^{-12}$ m^2/s after 438 days.



Effective chloride diffusivities (Fick's 2 law)

w/b %pozzolan	DCl,effx1E-12m2/s 35d	 9months	 14months
A 0.40 0%pozzolan	8.3	4.5	2.7
B 0.40 5%SF	2.1	2.0	1.3
C 0.40 5%SF,17%FA	1.2	1.6	1.5
	lab	field	field

Fig 10: Examples of the change in the effective diffusivity versus the exposure time in sea water; /10/. Three different concrete mixes. Water/binder ratio 0,40 in all concretes. SF=silica fume; FA=fly ash. Cement characteristics as in Fig 9.

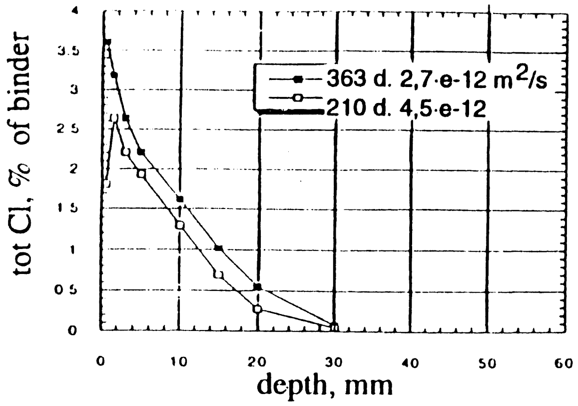


Fig 11: The chloride profile in a concrete exposed during 210 days and 363 days in sea water; /10/. w/c=0,40, No silica fume.

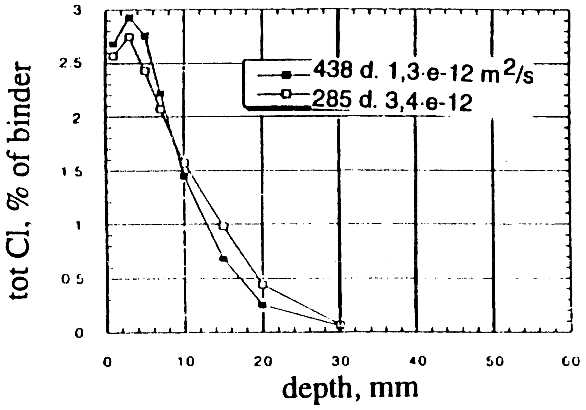


Fig 12: The chloride profile in a concrete exposed during 285 days and 438 days in sea water; /10/. Water/binder ratio 0,40, 5% silica fume.

5. The surface concentration of free chloride

Many observations have shown, that the *free* chloride at the surface of a concrete immersed in sea water, is higher than that in the surrounding sea water. It is not known whether the same is valid for concrete, that is only exposed continuously to de-icing salts. One example taken from from a marine structure (a quay) in Denmark exposed during 36 years in sea water is shown in Fig 13; /11/. The free chloride concentration in the submerged zone, and in the so-called "upper splash zone", is almost two times the outer concentration. Similar results have been found in Sweden /11/, in Japan /12/ and elsewhere. This phenomenon has not been explained. At a first sight, it seems impossible. It might be, however, that the presence of other negative ions play a rôle, primarily OH^--ions. If these are leached from the concrete, other negative ions, such as chloride, might enter the concrete in order to restore electrical equilibrium. If so, the "extra" chloride will not necessarily propel the diffusion. Another possibility is that the chloride is actually not "free", but adsorbed or bound in complexes of different kind. If so, they will not take part in, or force the diffusion. New observations, /18/, made under controlled conditions in the laboratory, indicate, that the internal chloride level is only 5% to 35% higher than in the surrounding solution, the level depending on temperature.

Fig 13 shows, that the surface concentation is considerably higher in the tidal water zone than in submerged concrete. The maximum value is about 5 times the concentration in sea water. The water/cement ratio in this structure is fairly high; 0,55. In a concrete of higher quality, e.g. with w/c-ratio 0,40, the capillarity is very low. It is, therefore, reasonable to assume, that the chloride accumulation in the surface is much smaller in such a concrete. The factor 5 between inner and outer free chloride concentration, therefore, ought to be the maximum possible in marine structures, and it is probably lower in high quality concrete.

In a structure exposed to de-icing salts, any value of the chloride concentration might occur at the surface; from saturation to zero. Probably, however, the driving concentration caused by de-icing salts, used during the winter season only, is normally lower than the driving concentration caused by continuous exposure to sea water.

In the next paragraph, it is assumed that the free chloride concentration in the surface of a marine structure is a certain multiple of the outer concentration in the surrounding water.

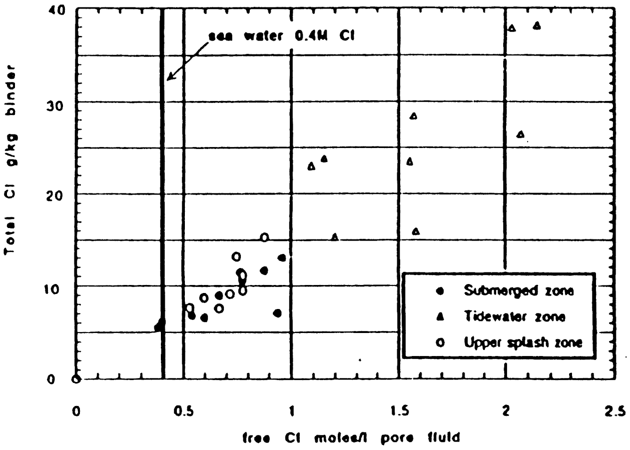


Fig 13: Relation between the free chloride in the pore solution, and the total chloride, in a concrete with w/c-ratio 0,55 exposed during 36 years in sea water; /11/. The outer chloride concentration is 0,40 mole/litres.

6. Time to start of corrosion

6.1 No leaching of alkalies. Pure Portland cement

It is assumed, that the chloride binding is linear, so that the normal solution to Fick's 2nd law can be used. Then, the diffusivity of free chloride is the same as the diffusivity of total chloride. This assumption, of linear binding, gives a calculated rate of penetration of the threshold concentration, that is bigger than that occurring in practice

The chloride concentration in sea water at the Swedish west coast is maximum 0,016 kg/kg or 0,46 mole/litre. The concentration of *free* chloride at the surface is supposed to be a multiple of this outer concentration. Thus, the free chloride concentration driving the diffusion is:

$$[Cl^-]_0 = \gamma \cdot 0{,}46 \text{ mole/litre } (= \gamma \cdot 0{,}46 \cdot 35{,}5 = \gamma \cdot 16{,}3 \text{ g/litre}) \qquad (5)$$

Where

$[Cl^-]_0$	the cloride concentration in the surface (mole/litre)
γ	the relation between free chloride in the surface of concrete and the chloride concentration of the surrounding sea water. Normally, $\gamma \geq 1$.

The concrete is assumed to be made by pure Portland cement of the same type as in the example above; Table 1. The water/cement ratio is 0,40. Then, the absolute minimum of the threshold concentration of *free* chloride is:

$$[Cl^-]_{thr} = 0{,}62 \text{ mole/l} \qquad (6)$$

It might very well be that the real threshold concentration of a concrete with the water/cement ratio of 0,40 is 2 or 3 times higher, or even more; see Fig 2.

The concrete, used in the example above, is assumed to have a cement content of 420 kg/m^3, and a water content of 0,4·420=168 litres/m^3. This means, that the concentration of chloride in the surface according to eq (5), and the threshold concentration of *free* chlorides according to eq (6) corresponds to the following values expressed as weight-% of the cement, and as weight-% of the concrete:

$$[Cl^-]_o=\{\gamma\cdot 16{,}3\cdot 168/420\cdot 10^3\}\cdot 100\% \;=0{,}65\cdot\gamma \text{ weight-\% of the cement} \qquad (7a)$$

$$[Cl^-]_o=\{\gamma\cdot 16{,}3\cdot 168/2400\cdot 10^3\}\cdot 100\%=0{,}114\cdot\gamma \text{ weight-\% of the concrete} \qquad (7b)$$

$$[Cl^-]_{thr}=[Cl^-]_o\cdot 0{,}62/(0{,}46\cdot\gamma)=0{,}65\cdot 0{,}62/0{,}46=0{,}88 \text{ weight-\% of the cement} \qquad (8a)$$

$$[Cl^-]_{thr}=[Cl^-]_o\cdot 0{,}62/(0{,}46\cdot\gamma)=0{,}114\cdot 0{,}62/0{,}46=0{,}154 \text{ weight-\% of the concrete} \qquad (8b)$$

One can now use the solution to Fick's 2nd law for calculation of the required effectice coefficient of chloride diffusivity for start of corrosion after 100 years, when the concrete cover is C. The solution can be written:

$$c/c_o=[Cl^-]_{thr}/[Cl^-]_o=\text{erfc}\{C/(4\cdot t_{life}\cdot D_{eff})^{1/2}\}=\text{erfc}\{\xi\} \qquad (9)$$

Where

c	the actual concentration of free chloride at depth C after time t_{life} (mole/litre) or (weight-%)
c_o	the concentration of free chloride in the surface (mole/litre) or (weight-%)
C	the concrete cover (m)
t_{life}	the required service life until start of corrosion (s). For 100 years, $t_{life}=3{,}153\cdot 10^9$ s.
D_{eff}	the effective chloride diffusivity during 100 years (m^2/s). D_{eff} is considerably bigger than the so-called "bulk diffusivity" determined on a young specimen at a traditional accelerated diffusion test.
ξ	a parameter that depends on c/c_o.

The argument x is tabulated in standard tables over the complentary error function (erfc); e.g. see Crank /13/.

For a concrete cover of 75 mm, a threshold concentration according to eq (6), and a surface concentration according to eq (5), the following relation is valid:

$$0{,}62/(g\cdot 0{,}46)=\text{erfc}\{0{,}075/(4\cdot 3{,}154\cdot 10^9\cdot D_{eff})^{1/2}\} \qquad (10)$$

Or:

$$1{,}35/\gamma=\text{erfc}\{6{,}677\cdot 10^{-7}/D_{eff}^{\,1/2}\} \qquad (11)$$

Corrosion is only possible when the following condition is fulfilled:
$[Cl^-]_{thr}<[Cl^-]_o$.

Then, the surface concentration must be at least 0,45 mole/litre, or γ must be at least 1,35.

In Fig 14 the solution of this equation is shown. In the figure is also shown the required diffusivity, under condition that the threshold concentration is, either 25 % higher, or twice the concentration given by eq (6).

Examples of maximum allowed chloride diffusivities in are shown in Table 2.

Table 2: Examples of maximum chloride diffusivities , that are allowed, if the service life shall be 100 years. Cement of the type described in Table 1. Cover 75 mm.

Threshold concentration $(\beta\cdot 0{,}62)$ 1) (mole/litre)	Maximum allowed chloride diffusivity, $m^2/s\cdot 10^{-12}$ Surface concentr. in multiples of the concentr. in the water $\gamma=1$	$\gamma=2$	$\gamma=3$	$\gamma=4$	$\gamma=5$
1·0,62 =0,62	0	5,0	1,5	1,0	0,73
1,25·0,62=0,78	0	24	2,6	1,3	1,0
2·0,62 =1,24	0	0	10	5,2	3,2

1) The constant β is a factor by which the calculated (minimum possible) threshold concentration 0,62 mole/litre is multiplied.

This means, that a maximum diffusivity of $5\cdot 10^{-12}$ m^2/s (158 mm^2/year) is required, if the surface concentration of free chlorides is twice the concentration of the surrounding sea water. If the surface concentration is 5 times that of sea water, a maximum diffusivity of $0{,}7\cdot 10^{-12}$ m^2/s (23 mm^2/year) is required.

These values are absolute maximum values, assuming a low threshold concentration of free chloride, corresponding to the criterion in eq (1). If this is increased, the required diffusivity is higher; already an increase of the threshold concentration by 25 %, to 1,25·0,62=0,78 mole/litr,e causes an increase in the required effective diffusivity to $24\cdot 10^{-12}$ m^2/s, and to $1\cdot 10^{-12}$ m^2/s for the surface concentration 2 and 5 times the outer concentration.

If the threshold concentration is twice the value given by eq (6), i.e. 1,26 mole/litre, corrosion cannot start when the surface concentration is twice the outer. For 5 times the outer concentration, a diffusivity of maximum $3\cdot 10^{-12}$ m^2/s is required.

The required diffusivity for other concrete covers, than 75 mm, can be calculated by multiplying the values obtained from Eq (11), or from the example above, by the factor $[C/0{,}075]^2$ where C is the new cover in m.

A reasonable maximum *effective* chloride diffusivity on the safe side is about:

* $1\cdot 10^{-12}$ m^2/s (30 mm^2/year) in the splash zone, where a certain accumulation of chloride can occur due to drying and wetting. It corresponds to a surface concentration of free chlorides, that is 5 times the concentration of sea water; see Fig 14. The threshold concentration is supposed to be 0,78 mole/litre, i.e. 25% higher than that given by eq (6).

* $5\cdot 10^{-12}$ m^2/s (160 mm^2/year) at the water level, where the concrete is saturated all the time. It corresponds to a surface concentration, that is twice the outer concentration in the sea water; see Fig 14. The threshold concentration is supposed to be 0,62 mole/litre given by Eq (6), which is a very pessimistic assumption.

These low effective diffusivities are evidently achieved in a concrete with a water/cement ratio of 0,40 after some years of exposure. Examples of this can be seen in Fig 8, 9 and 10. On the other hand, it can be difficult to obtain such low values at an accelerated "bulk diffusion test", in the laboratory, on specimens that are not exposed to natural conditions in the sea. Therefore, one can accept a somewhat higher value of the diffusivity in a laboratory test; especially when the concrete does not contain residual materials, such as fly ash or silica fume. For concretes containing these materials, the reduction in diffusivity in the practical use of the concrete seems to be lower. On the other hand, for such concretes, the initial value is also lower in most cases; see Fig 10.

NOTE: The cement in Fig 10, 11 and 12 is low in C3A, and has a fairly low alkali content. The C3A content is less than 2%. Despite this, the measured chloride diffusivity is very low. This confirms the observations made by many researchers during the last decade, that the C3A content is of little importance for chloride binding, and for the effective chloride diffusivity; e.g. see /14/. C4AF also plays a fundamental role and so does probably also physical characteristics of the cement paste formed.

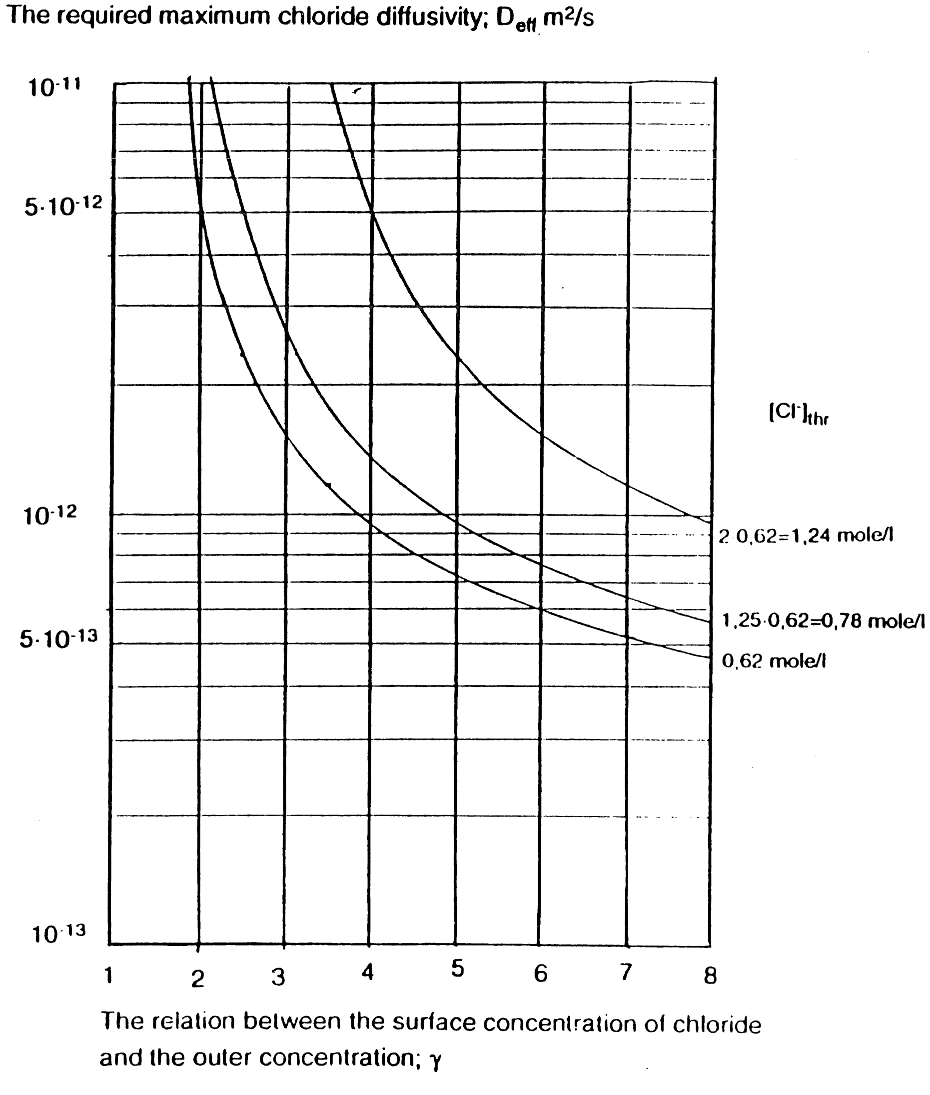


Fig 14: The required maximum effective chloride diffusivity for 100 years of service life of a concrete in sea water having a chloride content of 1,6 weight-%, (0,46 mole/litre), and 75 mm concrete cover.The surface concentration of *free* chloride is γ times higher than the outer concentration. The threshold concentration of *free* chloride is either 0,62 mole/litre, 0,78 mole/litre, or 1,24 mole/litre.

6.2 Alkalies are leached out

A: The threshold concentration is determined by the Hausmann criterion, Eq(1):

As shown in paragraph 3.2, the threshold concentration can not be lower than:
$[Cl^-]_{thr}$ = 0,019 mole/litre

Then, Eq (10) is changed to:

$$0{,}019/(\gamma\cdot 0{,}46)=\text{erfc}\{0{,}075/(4\cdot 3{,}154\cdot 10^9\cdot D_{eff})^{1/2}\} \qquad (10a)$$

Or:

$$0{,}041/\gamma=\text{erfc}\{6{,}677\cdot 10^{-7}/D_{eff}^{\ 1/2}\} \qquad (11a)$$

The following maximum diffusivities are valid for two surface concentrations, expressed in terms of the "concentration factor" γ; γ=1 and γ=2:

$\gamma=1$: $D_{eff} < 1{,}8\cdot 10^{-13}$ m²/s

$\gamma=2$: $D_{eff} < 1{,}4\cdot 10^{-13}$ m²/s

These values are very low, and are probably difficult to achieve in normal concrete, although field data indicate a very large reduction in the effective diffusivity over time; Fig 8-10. Probably, the complete leaching of alkalies assumed, does not occur in dense concrete at a depth as big as75 mm from the surface. There will probably be a diffusion of alkalies from the interior outwards, that compensates for the alkali migration to the surface.

B: The threshold concentration is higher than the Hausmann criterion:

In reality, the threshold concentration in dense concrete is higher than that predicted by the Hausmann criterion; Eq (1). A clear indication of this is given in Fig 2. Let us assume, that the threshold concentration according to Hausmann is increased by a factor β. Then, the following relation for the required diffusivity is valid, provided the concrete cover is 75 mm and the service life 100 years:

$$0{,}041\cdot\beta/\gamma=\text{erfc}\{6{,}677\cdot 10^{-7}/D_{eff}^{\ 1/2}\} \qquad (11b)$$

Examples of the application of Eq (11b) are shown in Table 2.

Table 2: Examples of maximum chloride diffusivities that are allowed if the service life shall be 100 years. Cement of the type described in Table 1. Concrete cover 75 mm. Alkalies are leached out.

Threshold concentration β[1]	Maximum chloride diffusivity, $m^2/s\cdot 10^{-12}$ Surface concentr. in multiples of the concentr. in the water γ=1	γ=2
1	0,18	0,14
5	0,55	0,33
10	1,11	0,55

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[1] The constant β is a factor by which the calculated (minimum possible) threshold concentration 0,62 mole/litre is multiplied.

These diffusivity values, for β=5 and β=10, are not lower than can be achieved in a concrete of high, but not extremely high quality.

6.3 Effect of mineral admixtures

The discussion so far refers to pure Portland cement. If a mineral admixture is added, the OH-concentration is reduced. An example of the effect of microsilica on the pH-value of the concrete is shown in Fig 3. Consequently, the threshold chloride concentration is reduced. This is clearly seen in Fig 2.

Let us assume that the ratio of the OH-concentration of the two types of concrete is:

$$[OH^-]_{PC+S} / [OH^-]_{PC} = \varepsilon \qquad (12)$$

Where $[OH^-]_{PC+S}$ is the OH-concentration of the concrete containing mineral admixture and $[OH^-]_{PC}$ is the OH-concentration of the pure PC-concrete.

Then, assuming the surface concentration is not changed, assuming 75 mm cover, assuming 100 years of service life, and assuming the same type of Portland cement as above, the following relation is valid:

$$\varepsilon\cdot(\beta\cdot 0{,}62)/(\gamma\cdot 0{,}46)=\mathrm{erfc}\{6{,}677\cdot 10^{-7}/D_{eff}^{1/2}\} \qquad (11c)$$

Where 0,62 is the threshold concentration defined by Hausmann for the pure Portland cement, 0,46 is the chloride concentration of the surrounding water. β is a factor expressing the fact that the real threshold concentration is higher than that given by the Hausmann criterion, ε is the reduction factor of OH-concentration defined by Eq (12), and γ is the "concentration factor" of chloride at the surface.

It is very much on the safe side to assume that $\beta=1$ and $\gamma=2$. Then, the following equation is valid:

$$0{,}674\cdot\varepsilon=\mathrm{erfc}\{6{,}677\cdot 10^{-7}/D_{eff}^{1/2}\} \qquad (11d)$$

This equation is applied to a concrete with 5% microsilica. The pH-reduction shown in Fig 5 is used. 5% Microsilica causes a reduction of the pH-value of about 0,25 pH-degrees; i.e. $\varepsilon\approx 0{,}5$.

Thus, the following maximum allowed diffusivity is valid for a concrete with and without 5% microsilica:

With microsilica: $D_{eff}<1\cdot 10^{-12}$ m^2/s

Without microsilica: $D_{eff}<5\cdot 10^{-12}$ m^2/s

According to this calculation, the effective diffusivity of a concrete with 5% microsilica must be reduced by a factor 5, compared with the PC-concrete, if the service life shall be 100 years for both concretes.

Conclusions

1: It seems reasonable to assume that a concrete with a water/binder ratio that does not exceed 0,40 and with a concrete cover that is not lower than 75 mm will sustain the marine environment during 100 years without corrosion of the reinforcement. Even under very pessimistic assumptions concerning the outer surface concentration of chloride, and concerning the threshold concentration, the maximum effective chloride diffusivity, that is allowed, is not lower than what will be reached in a high quality concrete of the type mentioned.

2: A laboratory chloride diffusion test, of the concrete to be used, is actually not required. If it is done, for example according to the test described in /9/, one shall consider that there is a big reduction in the diffusivity with time. It shall also be considered, that this reduction is probably bigger in a concrete without pozzolanic materials than in a concrete containing such materials. Reasonable reduction factors on the safe side are 10 for pure Portland cement concrete and 5 for concrete containing 5% microsilica (possibly the reduction is zero for a slag cement, and for a concrete containing both considerable amounts of silica fume and fly ash; see Fig 10). This means, that the requirement of the test result should be of the following order of size:

* $10 \cdot 10^{-12}$ m^2/s for pure Portland cement concrete
* $5 \cdot 10^{-12}$ m^2/s for concrete with 5% silica fume

Then, in both cases, the real effective diffusivity will not be higher than about $1 \cdot 10^{-12}$ m^2/s and probably at least 2 times lower.

3: There is no need for a lowest value of the C_3A-content of the Portland cement. An upper value of about 5% is needed, however, due to the risk of sulfate attack in sea water.

4: If all alkalies in the concrete are leached out, there will be a reduction in the threshold concentration, corresponding to a value, that is determined by the pH-value of calcium hydroxide; $\approx 12{,}5$. This means, that the maximum allowable chloride concentration is lowered to values of the order $0{,}1 \cdot 10^{-12}$ to $0{,}5 \cdot 10^{-12}$ m^2/s. It is, however, not likely, that complete leaching occurs at a concrete depth of 75 mm in a concrete with the water/cement ratio 0,40.

Note:The conclusions 1: and 2: are only valid under condition that the concrete is crack-free, and that it is absolutely frost resistant, and that the frost/salt surface scaling at the end of the 100 years is not more than about 10 mm; see/16/.

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