



PENETRATION RATE OF CHLORIDE IN MARINE
CONCRETE STRUCTURES.

Birgit Sorensen ¹ and Ernst Maahn ²

Dept. of Metallurgy, Technical University
of Denmark.



Abstract

Chloride penetration has been studied in some 15-20 years old concrete structures in the Danish Store Baelte area. The penetration follows an expression for diffusion in a semiinfinite system with constant surface concentration. The effective surface concentration is found to 0.12 - 0.77 wt% Cl and effective diffusion coefficient to range from 1.3 to 8.9×10^{-8} cm²/sec. The surface concentration decreases to the original chloride content from about 15 m above water-level. About 40% of total chloride is water soluble but this percentage decreases with decreasing total chloride content. The critical condition for corrosion in the reinforcement is found to be about 0.06 wt% chloride in the concrete (equal to approx. 0.12 g mol Cl⁻ pr litre in the pore water) but the corrosion attack is strongly dependent on the supply of oxygen.

Keywords: Concrete, chloride penetration, reinforcement, corrosion.

1. Now at: Statens Vejlaboratorium, Elisegårdsvej 5, 4000 Roskilde.

2. Now at: Korrosionscentralen, Park Alle 345, 2600 Glostrup

Introduction

In recent years, damage has been seen on several reinforced concrete structures in Denmark as well as in other countries. Cracks and spalling of the cover to reinforcement is often visible after a lifetime of a few years. Several causes of the damage have been suggested, bad workmanship often being mentioned as the most common reason. In many circumstances it seems clear, however, that corrosion in the reinforcement has accelerated or even initiated the damage.

In a high quality concrete made of Portland Cement, the reinforcement steel is protected by passivation due to the high alkalinity ($\text{pH} \approx 13$). However, unfortunately the passivity can break down either because of a decrease in the pH-value due to carbonation or because of penetration of activating ions, in practice chloride ions /1,2/. The iron will then show uniform corrosion or pitting depending on the circumstances. The corrosion transforms the iron into an oxide or a hydroxide form which gives rise to an increase in volume by a factor of up to about seven. This volume increase produces stresses in the cover with cracking and spalling as the ultimate result. It is well known that the carbonation is a rather slow process even at the optimum humidity about 50% RH /3/. Therefore, corrosion in reinforcement due to carbonation is normally observed only when the cover to the reinforcement is very thin, or when the concrete is inferior due to porosity, shrinkage cracks, etc.

The general use of concrete structures in marine environments as well as the increasing use of de-icing salt demands investigation of the rate of chloride penetration into concrete under known circumstances. The results presented here describe the rate of penetration of chloride in some Danish marine

structures up to twenty years old. The chloride is measured as total chloride, as water soluble chloride, and as free, water dissolved chloride in the porewater, and the penetration rate is related to the position over water-level and orientation. The quality of the concrete is also taken into account.

Experimental

The material examined comprises twenty eight drilling cores. Each core is 75 mm in diameter and 200-300 mm in length. The samples were removed from two harbour works and a bridge, all positioned in the Store Baelt area where the chloride content of the sea water is ~ 0.8 wt%. The 28 core samples were examined after the following scheme:

- Total chloride in 21 samples.
- Water soluble chloride in 3 samples.
- Chloride in pore water in 3 samples.
- Open porosity and specific gravity in 21 samples.
- Amount of mortar fraction in 21 samples
- Capillarity in 7 samples.

From each sample 4-8 disks of 10 mm thickness were cut using a dry carborundum cutter as illustrated in Fig.1. The discs were slightly ground and aggregate greater than 3 mm, was removed and chloride analysis was carried out on the mortar fraction.

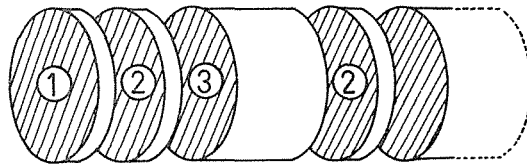


Fig. 1. Cutting scheme for drilling core.

1. outer disk (10-15 mm). Rejected because of carbonation.
2. disk (10 mm) used for chloride analysis.
3. intermediate piece, used for measuring of density and mortar fraction, and characterisation of coarse aggregate.

The total amount of chloride was analysed by extraction of the mortar fraction with boiling diluted nitric acid followed by potentiometric titration with AgNO_3 solution. From the weight proportion of mortar fraction, the results were calculated as weight % chloride in the concrete.

Water soluble chloride was determined by 16 hours extraction of the mortar fraction in distilled water at room temperature under a nitrogen atmosphere. The extract was analysed as before and results calculated as weight % chloride in the concrete.

The chloride concentration in the pore water was determined after 24 hours conditioning of a crushed sample at 100% RH under a nitrogen atmosphere. The pore water was squeezed out by means of a pressing tool and the pore water drop was buffered and analysed by a chloride selective electrode, in principle according to /4/.

The amount of mortar fraction was found after crushing, sepa-

rating a sample in a mortar fraction (paste + aggregate <3 mm) and a coarse aggregate fraction (>3 mm). The proportions in weight for the two fraction were used for the calculation of weight % chloride in concrete from the measured weight % chloride in mortar.

The capillarity was measured in the outer 5 - 10 cm of the drilling core. The cylindrical surface was sealed and the sample was conditioned for a minimum of 3 weeks at 73% RH. Capillarity number ($\text{kg/m}^2 \sqrt{\text{sec}}$) was then found by suction of water through the original surface for 1.5 hours /5/.

Results

It is possible to draw a curve (fig.2) showing chloride concentration versus distance from the original surface based on the chloride content found at different positions in the drilling core. It is assumed that the chloride penetration from the outer surface can be described by the error function solution to Fick's second law which is valid for the semiinfinite diffusion system. The mathematical expression for this system is:

$$C_x = C_s - (C_s - C_o) \operatorname{erf} \frac{x}{2\sqrt{Dt}} \quad (1)$$

where C_x = chloride concentration at distance x from the surface.

C_s = chloride concentration at surface, which is assumed to be a constant.

C_o = original chloride concentration in the concrete.

x = distance from the surface.

t = diffusion time which is equivalent to the age of the construction.

D = diffusion coefficient.

The penetration profile is determined by curve linear regression of Eq. (1) to the experimental results. The correlation coefficient between C_x and the error function solution is found in the range 1.000 - 0.987 which shows that Eq. (1) is a good approximation to the real progress of chloride penetration, see fig. 2.

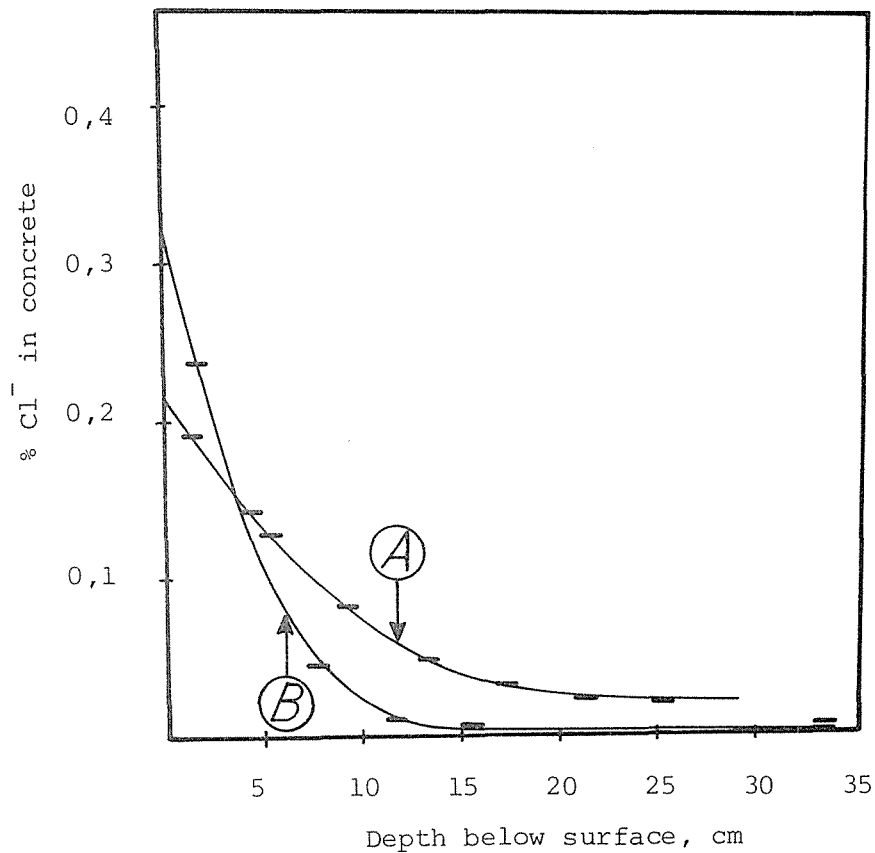


Fig.2. Examples of chloride penetration curves (total chloride).

A. Langeland Bridge, p11, 1962-1978, 1,8 m above water-level, East.
 $D = 8,1 \times 10^{-8} \text{ cm}^2/\text{sec}$, $C_S = 0,22\% \text{ Cl}^-$,
 $C_O = 0,02\% \text{ Cl}^-$.

B. Halsskov Harbour, 1958-1978, 1,5 m above water-level, Northwest.
 $D = 2,1 \times 10^{-8} \text{ cm}^2/\text{sec}$, $C_S = 0,32\% \text{ Cl}^-$,
 $C_O = 0,01 \text{ Cl}^-$.

No	place and orientation	build, year	height above waterlevel, m	C ₀ , % Cl ⁻	C _s , % Cl ⁻	Dx10 ⁸ cm ² /sec	density, g/cm ³	porosity, %	level for C _x = 0,06% Cl ⁻ , cm
1	Langeland Bridge, p7	1962	2,5	0,02	0,35	2,0	2,25	12,7	6,2
2	-	-	3,4	0,02	0,23	4,4	2,24	13,5	7,4
3	-	-	5,1	0,01	0,37	4,6	2,22	14,0	10,3
4	-	-	7,0	0,02	0,34	3,2	2,21	13,3	8,7
5	-	-	10,2	0,03	0,35	4,0	2,25	13,1	10,5
6	-	-	15,0	0,02	0,27	3,5	2,19	14,5	8,8
7	-	-	21,2	0,03	0,09	5,0	2,20	14,2	4,2
8	-	-	40 (1)	0,01	0,01				
10	-	-	1,8	0,02	0,22	6,1	2,22	13,7	12,0
11	-	-	1,9	0,03	0,20	4,8	2,24	14,3	9,2
13	-	-	2,0	0,02	0,14	8,1	2,24	13,6	9,0
15	-	-	1,9	0,02	0,12	8,9	2,28	13,0	8,4
N1	Stignæs Harbour	1967	2,2	0,01	0,24	2,6	2,25	14,2	5,5
N3	-	-	2,8 (2)				2,18	15,9	
G1	-	1962	1,8	0,09	0,65	2,0	2,31	10,7	
G2	-	-	1,2	0,00	0,77	2,3	2,31	10,9	8,7
A1	Halskov Harbour	1958	1,0	0,01	0,31	1,8	2,32	12,0	6,6
A2	-	-	1,5	0,00	0,20	2,3	2,27	12,7	5,9
B1	-	-	1,0	0,01	0,46	1,7	2,31	11,3	7,2
B2	-	-	1,8	0,01	0,32	2,1	2,30	11,8	7,2
C1	-	1962	2,3	0,01	0,15	1,3	2,31	11,0	3,2
C3	-	-	2,6	0,00	0,17	1,4	2,33	10,2	3,7

(1) analysis of carved samples.

(2) cracks has caused a diverging progress of chloridepenetration.

Table 1. Total chloride content in concrete, presented as effective surface concentration, effective diffusionkoefficient, and the level of a chloridekoncentration of 0,06% Cl⁻.

By curve linear regression, C_s , C_o and D are determined for each drilling core as shown in Table 1.

Fig.3. shows the concentration of water soluble chloride with distance from the surface. The relative amount of water soluble chloride to the total amount of chloride ranges from 30 to 70% and it increases with increasing total amount of chloride.

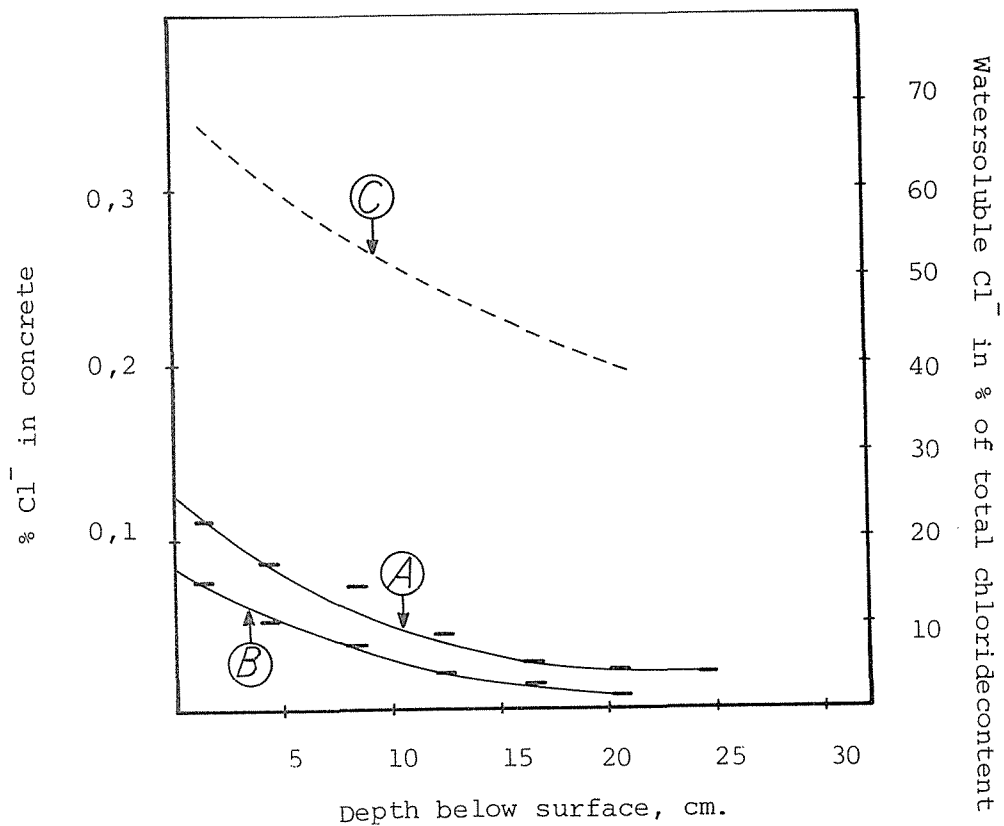


Fig.3. Langeland Bridge, p11, 1962-1970. 1,9 m above water-level, Northwest

- A. Total chloride.
- B. Water soluble chloride.
- C. Relative amount of water soluble chloride to total chloride.

The chloride concentration in pore water varies with distance from surface as shown in fig.4. The concentration of chloride in pore water ranges from 0.6 to 0.005 mol/l which is equal to a variation from 10 to 70% of the total amount of chloride in the concrete.

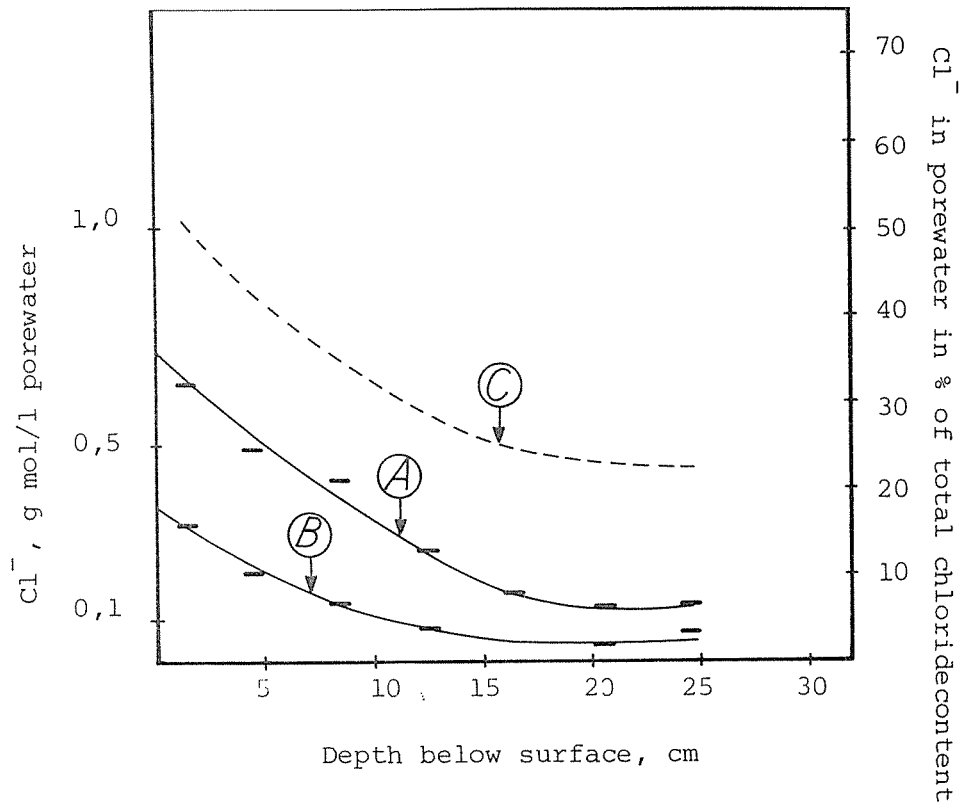


Fig. 4. Langeland Bridge, p11, 1963-1978, 1,9 m above water-level, Northwest.

- A. Total chloride, calculated as mol Cl⁻/l pore solution.
- B. Measured chloride concentration in pore solution.
- C. Relative amount of chloride in pore solution to total chloride.

The chloride distribution found in the twenty one drilling cores shows that the chloride penetration can be approximated by a semiinfinite diffusion system, which means that the penetration of chloride is completely determined by three para-

meters: the initial concentration in the concrete C_0 , the effective surface concentration C_s , and the effective diffusion constant D .

The initial concentration C_0 depends on the materials used as the chloride originates from the water, marine materials or additives.

The diffusion constant, D , found here is an effective value or mean value over time and location. With time, there are variations in temperature and humidity which have an influence on the value of D , but as the three examined constructions are situated in the same geographical area, these factors will be the same for all samples and therefore, the diffusion constants are comparable. The diffusion constants found here, ranging from 1.3 to $8.9 \times 10^{-8} \text{ cm}^2/\text{sec}$, are in good agreement with results presented by Colleparidi et al. /6/ of $1.7 - 3.2 \times 10^{-8} \text{ cm}^2/\text{sec}$ and by Kondo et al. /7/ with $7 \times 10^{-8} \text{ cm}^2/\text{sec}$.

Beaton et al. /8/ found penetration in drilling cores equal to a diffusion coefficient of $2 \times 10^{-8} \text{ cm}^2/\text{sec}$ while Institut TNO /9/ found lower penetration rates, equivalent to $D = 0.5 - 1.0 \times 10^{-8} \text{ cm}^2/\text{sec}$.

It is assumed that the diffusion coefficient of chloride ions depends on the quality of the concrete. The porosity, which is related to the water/cement ratio, must be decisive but also the amount and quality of aggregate as well as cement is supposed to influence the diffusion coefficient. It has not been possible to obtain the initial data for the constructions in question so the concrete quality is described by density, open porosity, capillarity number, and amount and type of coarse aggregate.

From fig. 5 it is seen that the diffusion coefficient increases with increasing porosity but the data for "p11", Langeland Bridge suggest that other factors also have an influence.

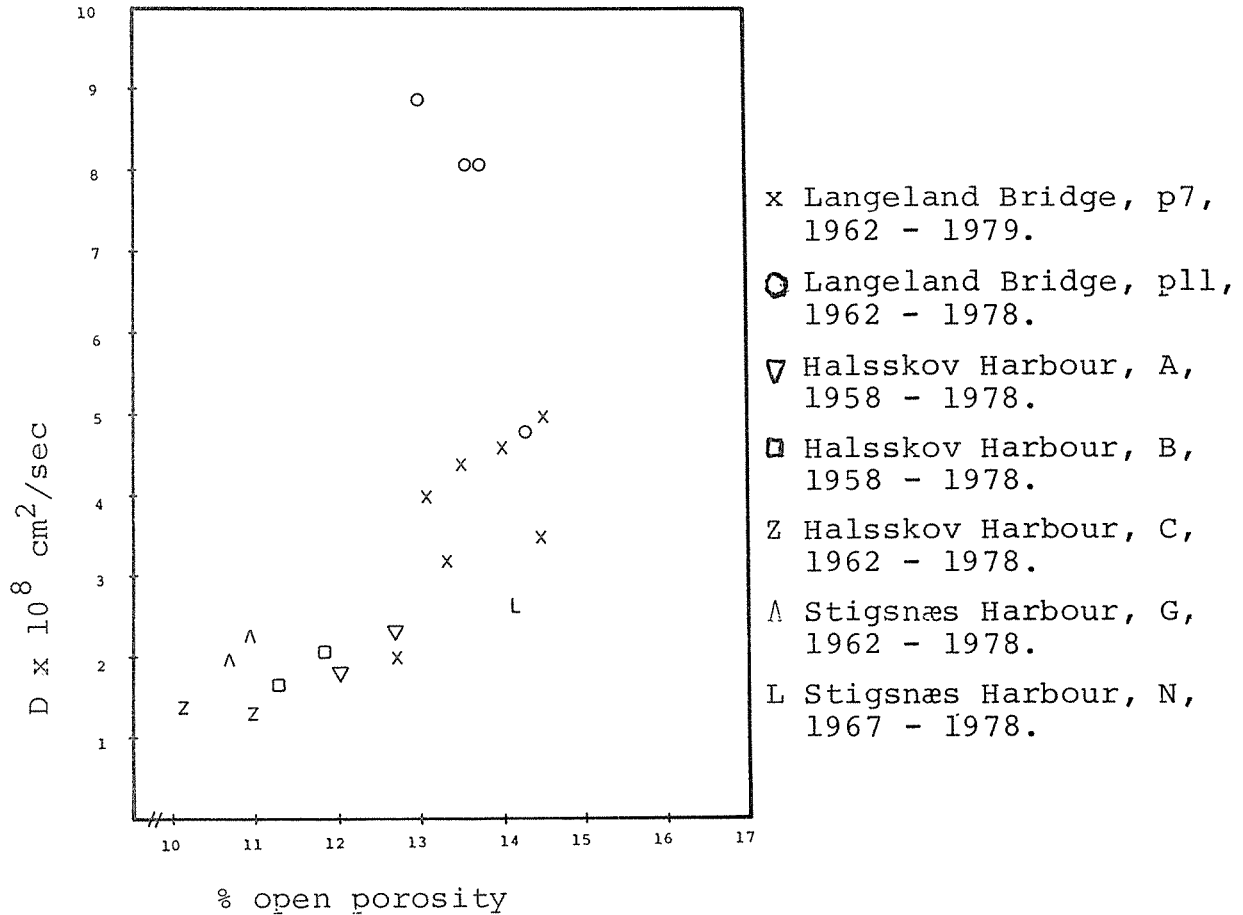


Fig. 5. Diffusion constant versus open porosity of concrete.

A significant relation between diffusion coefficient and capillarity was not observed. However, this is not surprising as the water suction is measured through the original surface and this surface will change in time because of carbonation, salt penetration, fouling etc. thus, the capillarity number can not be considered as an characteristic constant for the concrete material.

The effective surface concentration of chloride C_s is an in-

teresting parameter which characterizes the availability of the salt in the environment. A strong variation in C_s - value between the measuring points was detected. It is assumed that there is a dependence on local conditions like sea traffic, shelters etc. but there is also a significant dependence on geographic orientation which must be explained by the prevailing western wind and the sun. These factors give rise to variation in wetting from sea water and rain water as well as degree and duration of dry and wet periods.

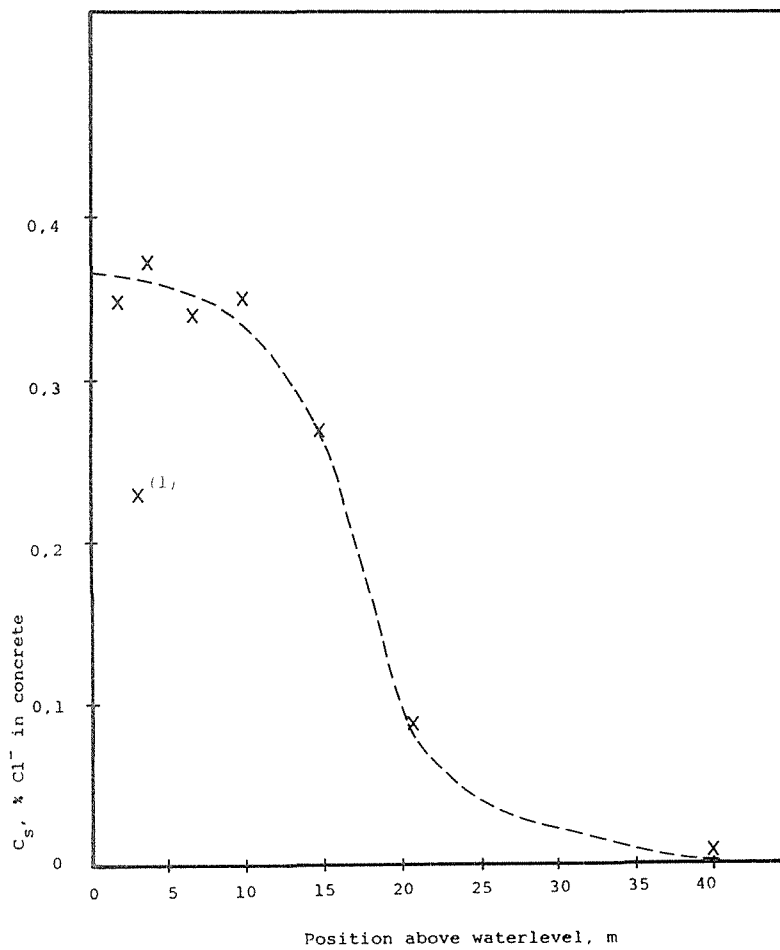


Fig. 6. Effective surface concentration of chloride, C_s , as a function of position above water-level. Langeland Bridge, p7, 1962-1979, east.
(1) sheltered area.

The relation between C_s and position above the water-level is shown in Fig. 6. The C_s - value is nearly constant up to 10 - 15 m above the water-level and only then is there a drop in the surface activity of chloride. This level is well above the splash zone and, thus, the surface concentration must be maintained by sea-fog.

Corrosion Aspects.

The penetration of chloride into concrete is described on the basis of analysis of the total chloride content. However, only part of this chloride is dissolved in the pore water and, thus, is aggressive with respect to corrosion of the reinforcing steel. The amount of chloride, which is chemically bound, (e.g. as Friedel's salt or calcium silicatehydrate) is strongly dependent on, among other things, the cement type and, therefore it would be desirable to have a measure based on dissolved or water soluble chloride for the chloride concentration which is critical with respect to corrosion.

The two methods used here for determination of accessible chloride are both rather uncertain. With the material here it is not possible to differentiate between chloride found by water extraction and chloride found by analysis of pore water pressed from the concrete, but it is seen that the ratio of free chloride to total chloride is smaller at low total chloride levels than at the higher chloride levels. This indicates that the concrete attains saturation in chemically bound chloride and further chloride will remain in dissolved or soluble form.

Several investigators /10-16/ have tried to determine the critical total content of chloride with respect to corrosion but, as expected, there is considerable scatter in the published results. Older investigations specify the critical content

0.5 - 2.0 wt% chloride in concrete while newer results indicate the critical level as low as 0.03 - 0.08 wt%.

Considering a critical value of 0.06 wt% Cl^- , it is seen that this value is found in the examined constructions in the range 3 - 12 cm below the surface (Table 1) which is equal to the position of the outermost rebars.

no	depth, cm	corresponding chloride content, %	condition of iron
1	5	0,11	3
2	5	0,12	2
3	5	0,19	3
4	5	0,15	2
5	5	0,17	2
6	5	0,12	2
7	5	0,06	2
10	7	0,11	2
N1	9	0,02	1
N3	9	0,10	4
G1	9	0,11	3
G2	9	0,05	1

Table 2. Condition of reinforcement iron found in drilling cores. Depth is the distance from original surface to position of iron.

1. no corrosion
2. light stain
3. slight corrosion
4. severe corrosion

The degree of corrosion attack was estimated for the rebars found in the drilling cores and in Table 2 the degree of corrosion is correlated to the chloride content found at the position of the rebar. Only two pieces of rebar placed at the lowest chloride content were totally free from corrosion. The larger part of the specimen shows a slight corrosion attack but it can be assumed that the corrosion here had been controlled by the supply of oxygen. In one case (N3) cracks were found in the concrete near the rebar and, there, heavy corrosion attack was observed which shows that the combination of a chloride level of 0.10 wt% and an ample supply of oxygen is dangerous with respect to corrosion on the iron.

It is reasonable to assume that a better criterion for the critical chloride concentration with respect to corrosion could be based on the determination of water soluble chloride or the chloride concentration in pore solution. Such a criterion has not yet been established, but experiments /15-20/ with saturated calcium hydroxyde solutions show critical chloride concentrations ranging from 0.007 to 0.04 mol/l. The corrosive environment in concrete can be rather different in both chemistry /21/ and transport conditions from that in the solutions used in these experiments and it is probable that the concentrations mentioned here are too low to be the critical level for concentration of chloride dissolved in the pore water. Assuming a critical total chloride content of 0.06 wt% as mentioned earlier and 40% of the chloride dissolved in the pore water, it can be calculated that the critical pore water concentration is about 0.12 mol Cl^- /l and this level seems more consistent with the results found in this work.

Conclusion

It has been shown that the chloride penetration in concrete can be described as a semiinfinite diffusion system. The effective surface concentration depends on local circumstances but was almost constant up to 10 - 15 m above water-level.

The effective diffusion coefficient shows little variation from point to point in the individual constructions. There is a greater variation from one construction to another, and this variation must be explained by variation in porosity as well as type of aggregate used.

If the total chloride concentration of 0,06 % is considered as critical for corrosion, the critical concentration is found in a depth of 5 - 10 cm below surface after about 18 years, provided the concrete is in good condition without macro cracks, and the position is less than 15 m above water-level.

References:

- /1/. M. Pourbaix, Corrosion Vol. 25, No. 6 (1969).
- /2/. M. Pourbaix, Lectures on Electrochemical Corrosion, Plenum Press 1973.
- /3/. Pihlavajavaara, Concrete Seminar, Helsinki 1974.
- /4/. K. Tutti, Korrosion på stål i betong, Cement- og Betonginstituttet, rap.nr. FO 8101.
- /5/. Betonbogen, CTO 1979, chapt.3.
- /6/. M. Collepardi, A. Mareilalis, R. Turriziani, Journal of the American Ceramic Society, Vol 55, No 10 (1972).
- /7/. R. Kondo, M. Satake, H. Ushiyama. The Cement Association of Japan. Review of 28. General Meeting, May 1974.
- /8/. J.L. Beaton, D.L. Spellman, R.F. Stratfull, Corrosion of Steel in Continuously Submerged Reinforced Concrete Piling. California Division of Highways, Report No M&R 635116 (1967).
- /9/. Instituut TNO Voor Bouwmaterialen en Bauwconstructies, Onderzoek naar de Duurzaamheid van 5 Sluizen in Zeeland, Report No B-79-152 (1979).
- /10/. V.K. Gouda, Br. Corr. Journal, Vol 1, No 4 (1966).
- /11/. J.R. Van Daveer, ACI Journal, No 12 (1966).
- /12/. K.C. Clear, R.E. Hay, FHWA-RD 7332, 1973.
- /13/. Rielem Technical Committee CRC, Matériaux et Construction Vol 9, No 51 (1976).
- /14/. A. Baumel, Zement-Kalk-Gips, No 7 (1959).
- /15/. A.D. Lewis, 1. International Congress on Metallic Corrosion, 1961.

- /16/. B. Sørensen, Korrosion af varmforzinket armeringsjern. Thesis, DTH 1981.
- /17/. D.A. Housmann, Materials Protection, Vol 6, No 11 (1967).
- /18/. K.S. Rajagopalan et Al., J. Scient. Ind.Res. Vol 28, No 10 (1969).
- /19/. H. Polster, J. Kunscher, Baustofindustrie No 1 (1974).
- /20/. W.L. Sluijter, P.C. Kreijger, Heron Vol 22, No 1 (1977).
- /21/. P. Longuet, Silicates Industriels, No 7-8, (1976).