

Chloride ingress data from field and laboratory exposure – Influence of salinity and temperature

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Abstract

Marine exposure conditions provide an aggressive environment for reinforced concrete structures, mainly due to the occurrence of chloride-induced reinforcement corrosion. There are several influencing factors, but despite a lot of research little is known about the influence from variations in the exposure conditions. Therefore an exposure programme has been made, where concrete specimens, made from one single concrete composition, have been exposed at 12 marine locations around the world, along with a parallel study under laboratory conditions. The specimens have been constantly submerged during the exposure to get well-defined exposure conditions. The purpose was to get a quantitative measure of how different exposure conditions influence the durability of reinforced concrete, measured in terms of chloride ingress into the concrete. The results indicate that the exposure conditions (salinity and temperature of seawater), as expected, influenced the chloride ingress. This is further analysed and discussed in the paper.
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1. Introduction

The service life of reinforced concrete structures in marine conditions is to large extent influenced by the occurrence of chloride-induced reinforcement corrosion. Chlorides from seawater penetrate into the concrete, reach the reinforcement and after a certain time the chloride content exceeds a critical level, i.e. the chloride threshold level, and corrosion is initiated. However, there are some other requirements that also must be fulfilled to achieve an ongoing corrosion process, e.g. sufficient supply of oxygen, to enable the oxidation, and presence of electrolyte, to enable formation of an electrical circuit.

Mathematical models have been developed to predict the durability of reinforced concrete, mainly chloride ingress into concrete, and how this influences the service life of the structures. In these models the influences on

the durability from different factors are mathematically described. The main influencing factors are: (i) selected material qualities, (ii) workmanship during construction and (iii) exposure conditions. Despite a lot of research little is known about the last of these factors. In best case the influence from the environmental actions is quantified with chloride ingress data measured in concrete exposed at different locations, cf. [1]. However, usually these kinds of data are measured in similar concretes exposed at one, or in some rare cases two, locations. This means it is difficult to compare chloride ingress measured in different concretes exposed at different locations, since the chloride ingress will be influenced by an interaction of the concrete properties and the exposure conditions. A comparison may therefore result in a large scatter, as for example described by Lindvall and Nilsson [2].

Thus, there is a need to separate the influence from exposure conditions and concrete properties. Therefore, an exposure programme has been made to investigate differences in chloride ingress between different marine exposure locations. The aim has been to determine how different

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exposure conditions influence the chloride ingress into concrete, excluding the influence from the concrete properties. For this purpose concrete specimens have been exposed at 12 different locations around the world. Parallel with the field exposure specimens have been exposed in the laboratory in salt solutions. After finalized exposure, the chloride ingress into the concrete has been determined. A short review of the programme and the results is given in this paper – a more detailed description is given in [3,4].

2. Exposure programme

2.1. Materials and specimens

The concrete composition used in the exposure programme is presented in Table 1. To minimise any effects due to variations in the materials used for the concrete all castings have been made with cement from only one delivery from the cement factory, aggregates from the same two deliveries (sand and gravel) and air entraining agent from only one bottle.

The concrete specimens used in the exposure programme measure $150 \times 150 \times 75 \text{ mm}^3$. After casting the concrete was cured for three days in the moulds, before de-moulding, and then wrapped in a plastic cover and

stored in a controlled climate room ($+20^\circ\text{C}$ and $50\%\text{RH}$) to an age of at least 28 days. After the curing, the specimens were prepared and then finally stored in the controlled climate room ($+20^\circ\text{C}$), under a plastic cover to prevent drying, before exposure. During transport to the exposure locations the specimens were wrapped in plastic to prevent drying. Consequently the initial conditions before exposure of the concrete were self-desiccation without any significant drying to the surroundings, for at least a month. To get a well-defined surface, without any effects from the mould etc, only chloride ingress through sawn surfaces on the specimens has been studied.

2.2. Field exposure

The exposure was made at 12 different locations around the world and to get well-defined exposure conditions the exposure has been made constantly submerged, i.e. the concrete has been covered by seawater. The geographical locations of the exposure locations are shown in the map in Fig. 1 (together with information about number of specimens exposed).

The exposure at all location was started in 2000 and ended in 2001. The exact dates for the beginning and end of the exposure at each location are given in [3]. The

Table 1
The concrete composition used in the exposure programme

Material	Amount (kg/m^3)	Density (kg/m^3)	Volume proportion (–)
Cement (CEM I 42.5 BV/SR/LA)	450	3105	0.143
Sand (0–8 mm)	938	2650	0.354
Stone (8–16 mm)	745	2650	0.281
Water (tap water) ($w/b = 0.40$)	180	1000	0.180
Air ^a	–	–	0.045

CEM I 42.5 BV/SR/LA – (Swedish Cementa Anläggningscement Portland Degerhamn).

^a The air content in the concrete is regulated by adding AEA (Cementa L 14) – dosage 0.030% of cement weight.



Exposure locations:

1. Banyuls sur Mer (France). 5+4 specimens.
2. Cascais (Portugal). 5 specimens.
3. Dubai* (United Arab Emirates). 5 specimens.
4. Eastern Scheldt (Netherlands). 5 specimens.
5. Hirtshals (Denmark). 4 specimens.
6. Hvalfjörður (Iceland). 5 specimens.
7. Isle of the Dead* (Tasmania, Australia). 4 specimens.
8. Kjøpsvik (Norway). 5 specimens.
9. Källhamn (Sweden). 5 specimens.
10. La Rochelle (France). 5 specimens.
11. Skanör (Sweden). 5 specimens.
12. Träslövsläge (Sweden). 6 specimens.

* : Outside map.

Fig. 1. The geographical locations of the exposure locations in the exposure programme. Map downloaded from [5].

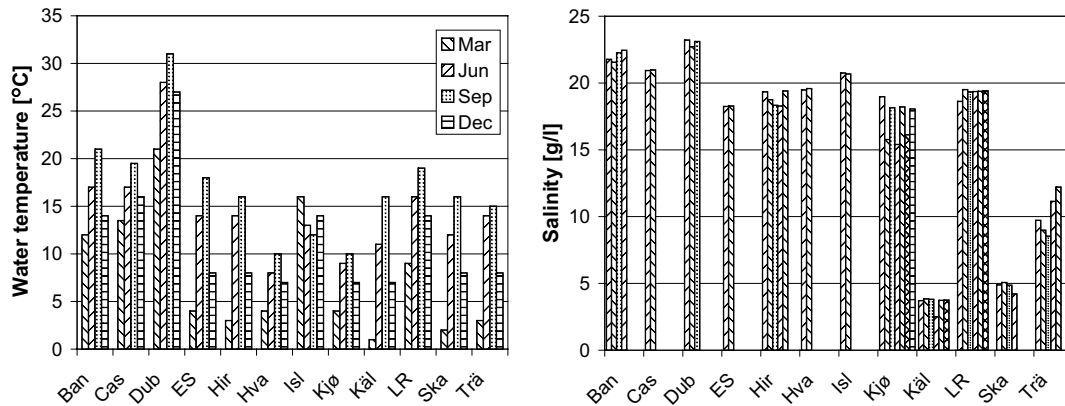


Fig. 2. Exposure conditions – salinities (right) and temperature (left) in seawater. Temperature data from [6].

exposure conditions have been investigated in terms of chemical composition and temperature of the exposure water, see Fig. 2. The names of the locations have been abbreviated, due to space limitations. The water temperatures are given as monthly mean values at the water surface, i.e. depth 0.0 m, based on data from [6]. The salinity of the seawater has been analysed from water samples taken from each exposure site. Each column in Fig. 2 (right) represents a measurement from one water sample taken during the exposure. The time intervals for the water samples are not the same for the different exposure sites, which means that the variations in salinities between different locations cannot be directly compared.

In Fig. 2 (right) it can be observed that salinity in the seawater is fairly constant except in Kjøpsvik, Skanör and Träslövsläge on the Swedish west coast. From Fig. 2 (left) it can be observed that the temperature of the seawater varies with an annual cycle.

2.3. Laboratory exposure

Parallel with the field exposure specimens have been exposed in the laboratory. The exposure has been in submerged conditions in salt solutions prepared with de-ionised water and sodium chloride (NaCl). The salt solutions had two different salinities, 8.3 g NaCl/l (5 g Cl⁻/l), representing the conditions in the Baltic Sea, and 33.0 g NaCl/l (20 g Cl⁻/l), representing the conditions in the Atlantic Ocean, and two temperatures: +7 °C and +20 °C.

3. Measurement techniques

After the exposure the specimens were cleaned from marine growth and transported to the laboratory. Before the transport the specimens were dried in the air, to let surface water dry away, and then packed in plastic bags which were sealed to prevent uncontrolled drying and a transport of chlorides. In the laboratory, cores were drilled from the centre of each sawn surface and powder samples were collected from different depths by means of thorough profile grinding.

The powder samples have been analysed for acid-soluble chlorides and calcium, analysed with potentiometric titration. The total chloride content in the concrete has been determined. The binder content in each sample was determined from the analysed calcium content, since the calcium content in the aggregate is negligible. The calcium content in the cement used in the concrete has been 64.9%. The results are presented as measured chloride ingress profiles, where the quotient between the chloride and binder content is presented in depth intervals. A more detailed description of the analysing procedure is given in [3].

4. Results

4.1. Laboratory exposure

In Fig. 3 the measured chloride ingress profiles from the laboratory exposure are presented. For clarity only the means profiles (from four different exposure conditions) are presented in the figure. The exposure conditions (5 and 20 g Cl⁻/l and 7 °C and 20 °C) are indicated in Fig. 3. The exposure times were between 413 and 422 days.

From the results presented in Fig. 3 it can be observed that the chloride ingress seems to be mainly influenced by the salinity and only to a small extent of the temperature

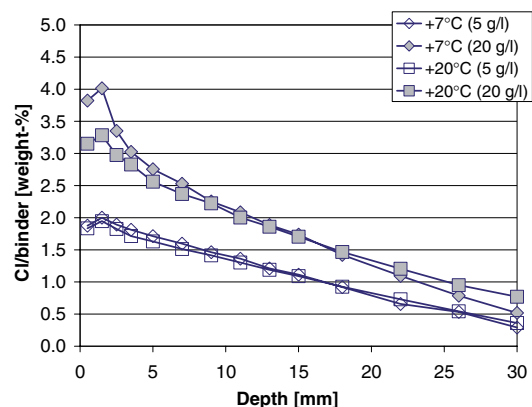


Fig. 3. Chloride profiles from laboratory exposure – mean profiles.

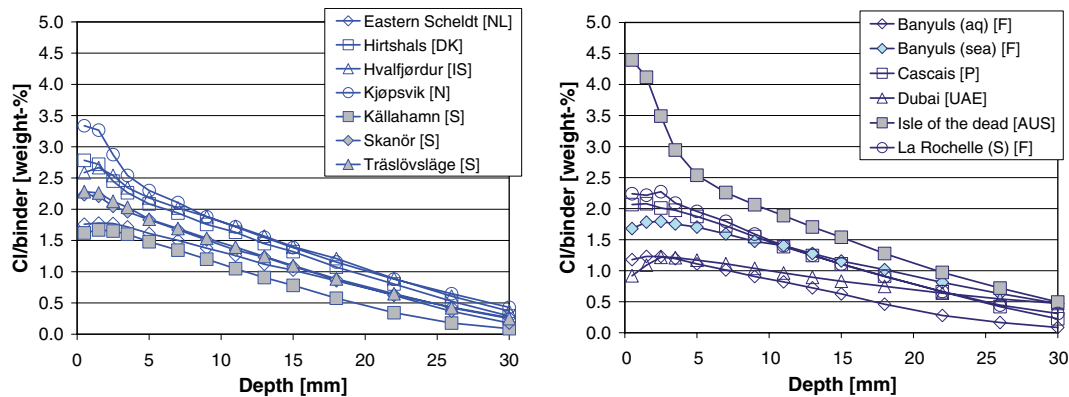


Fig. 4. Mean chloride profiles – cold (left) and warm locations (right).

of the exposure solution. This is opposite to the findings from the field exposure made at the different marine locations, presented in Fig. 4. This is further discussed in Section 5.

4.2. Field exposure

The measured chloride ingress profiles from the field exposure are presented in Fig. 4. For the sake of clarity mean profiles from each exposure location are presented in Fig. 4. A division has been made into cold and warm exposure locations (annual mean water temperature below or above +14 °C respectively), which are presented to the left and right in Fig. 4 respectively. The exposure times were around one year for all exposure locations.

By comparing the mean chloride ingress profiles presented in Fig. 4 it can be studied how the salinity and temperature of the seawater influence the chloride ingress. The influence of the water temperature can be observed by comparing the profiles from cold and warm locations. In cold locations the surface chloride contents are somewhat higher while chloride contents at larger depths are somewhat lower compared to the warm locations. The influence from the salinity of the seawater can be studied by compar-

ing the cold locations with the ones along the Swedish coastline, i.e. Källahamn, Skanör and Träslövsläge.

5. Analysis and discussion

5.1. Uncertainty in measured chloride ingress profiles

The uncertainty in the measurements of chloride ingress has been analysed by calculating the coefficient of variation (COV) for each depth in the measured chloride ingress profiles from the field exposure. COV has been determined by dividing the mean with the standard deviation of the chloride content at each depth. In Fig. 5 COV for the chloride ingress profiles in Fig. 4 are shown – cold and warm locations are presented to the left and right respectively.

As seen in Fig. 5 the coefficient of variation varies over depth. Close to the surface (up to depths of 5 mm) COV is large due to surface effects, in some cases up to 50%. At depths over 20 mm COV is also large, in some cases over 50%, since the measured chloride contents are small and thus have large relative uncertainties. Between 5 and 20 mm COV is between 10% and 20% for all locations. Similar results have been obtained from the laboratory exposure, except that COV is somewhat lower. These COVs should reflect the accuracy in the determined

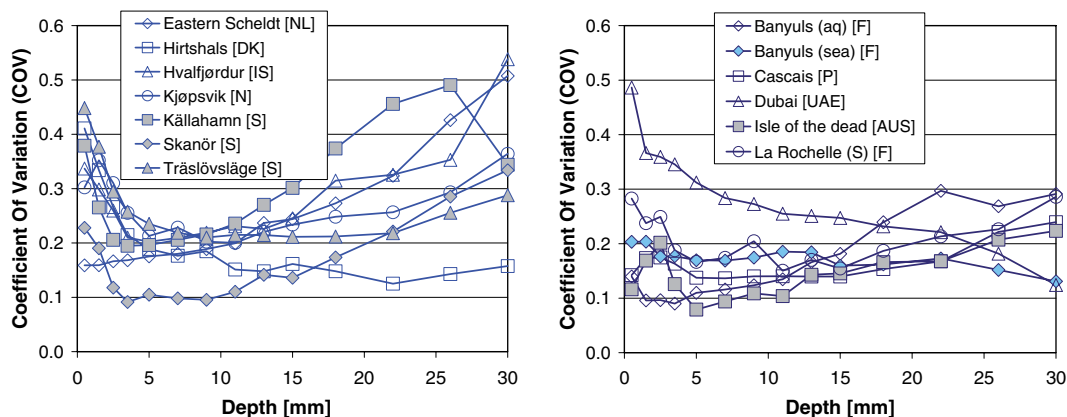


Fig. 5. COV for the measured chloride content – cold (left) and warm locations (right).

chloride content in the concrete, since the exposure conditions should not vary significantly at one exposure location. Thus the accuracy of the measured chloride ingress profiles depends on the level of the chloride content, where the accuracy gets worse when the chloride content decreases. Generally the COV of the measured chloride content is 10–20%, but with low chloride contents COV increases to over 50%.

The measured chloride ingress profiles have been evaluated with the error-function solution to Fick's second law, to achieve the regression-parameters, C_{sa} and D_{F2} (apparent surface chloride content and chloride diffusion coefficient respectively). The uncertainty in C_{sa} and D_{F2} have been examined in terms of COV, where COV has been found to vary for D_{F2} between 8.6% and 34.9% and for C_{sa} between 8.0% and 33.0%.

5.2. Effect on chloride ingress of salinity and temperature of exposure water

The effect on chloride ingress of the salinity and temperature of the exposure water has been investigated. For clarity the different exposure locations have been grouped into classes, based on the annual mean salinity (AMS) of the exposure water: BS+ÖS (Exposure in the Baltic Sea and in Öresund. AMS \approx 3–5 g/l), KG (Exposure in Kattegat. AMS \approx 10 g/l), KV (Exposure in Kjøpsvik. AMS \approx 17 g/l), Rest (Exposure at the rest of the exposure locations. AMS \approx 18–23 g/l) and Lab (Exposure in the laboratory. AMS \approx 5 g/l and 20 g/l). In Fig. 6 the effects of the temperature of the seawater on C_{sa} (left) and D_{F2} (right) are shown. Trend lines (for salinities of 5, 10 and 20 g/l) are added to the figures to describe how C_{sa} and D_{F2} vary with temperature, based on the Arrhenius equation. Only data from the field exposure have been used to evaluate the trend lines.

From Fig. 6 it can be seen that the temperature of the exposure water seems to have significant effect both on C_{sa} and D_{F2} evaluated from the results from the field exposure, where C_{sa} decreases and D_{F2} increases with increasing temperature. The salinity of the seawater seems

to have only limited effect both on C_{sa} and D_{F2} . However, most of the data used for the evaluation of the trend lines come from exposure in seawater with an annual mean temperature of 10–17 °C, which means it may be difficult to establish statistically meaningful trends above these temperatures. Anyhow the trend lines established in Fig. 6 will be used for the further analysis. However, more research is needed to better clarify which effect the temperature has on the chloride ingress into concrete also in other temperatures than the ones investigated in the present study.

An explanation to the results presented in Fig. 6 can be a temperature effect on the chloride binding, where the chloride binding decreases with increasing temperature, [7], i.e. the content of bound chlorides C_b decreases. This would mean that D_{F2} does not have a temperature dependency of its own, but it can be attributed to the temperature dependency of the total chloride content, C_{tot} , (or the bound chlorides, C_b), where C_b and C_{tot} decreases with increasing temperature. The temperature effect on C_{tot} can also explain the temperature dependency of C_{sa} , where C_{sa} consequently should decrease with increasing temperature. This is also supported by the data presented in Fig. 6 (left), where C_{sa} decreases with increasing temperature. The temperature effect on the chloride binding and how it influences the results from the exposure programme is further discussed in [3].

If the results from the field and laboratory exposures are compared a difference in influencing factors can be observed, cf. Figs. 3 and 4. In field conditions the main influencing factor was the temperature of the seawater, while in laboratory conditions the salinity was the main influencing factor. A possible explanation for this observation could be differences in exposure conditions, e.g. the pH of the exposure solution, which may influence how chlorides penetrate into and are bound in the concrete. Despite the fact that the exposure solutions in the laboratory exposure were changed every week pH in the solutions was over 10 almost immediately after the solution was changed. In seawater pH normally varies between 7 and 8, and thus there is a difference in the exposure conditions between field

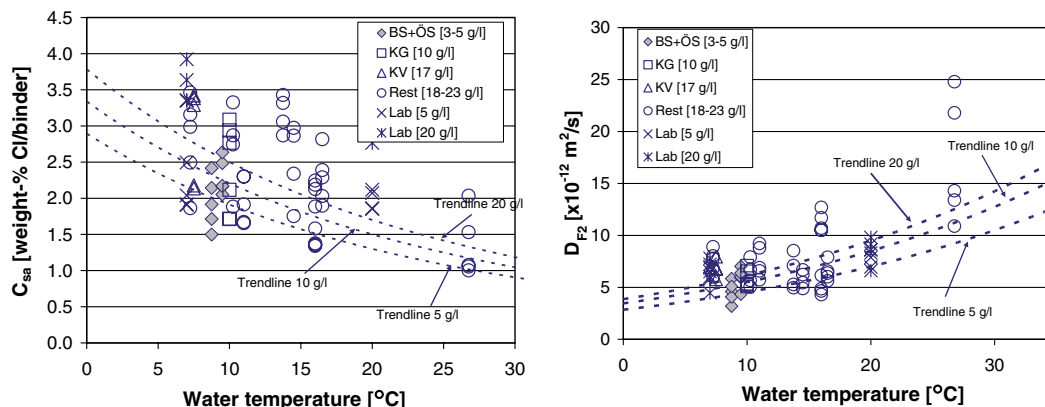


Fig. 6. The effect of the salinity and temperature on C_{sa} (left) and D_{F2} (right).

and laboratory exposure, which may explain the observed difference in chloride ingress.

6. Conclusions

The following conclusions have been drawn from the exposure programme, which considered one concrete composition:

- *Uncertainty in measured chloride ingress profiles.* The measured chloride ingress were found to have an uncertainty, in terms of coefficient of variation (COV), varying between 10% and 20% and up to 50% in parts of the concrete with low chloride content. There is also an uncertainty in the evaluated parameters C_{sa} and D_{F2} , where COV has been found to vary for D_{F2} between 8.6% and 34.9% and for C_{sa} between 8.0% and 33.0%. The observed uncertainties on C_{sa} and D_{F2} may give a significant influence on predictions of chloride ingress, and therefore this uncertainty should also be considered in predictions.
- *Effect of salinity and temperature of exposure water.* In field conditions the main influencing factor on chloride ingress into concrete was the temperature of the seawater and the salinity of the seawater did only have a subordinate effect. However, it should be kept in mind that these conclusions have been drawn from measurements of the total chloride content in concrete, which means that they reflect the combined effect of the salinity and temperature on the chloride binding and transport. If the effects on the bound or free chloride content had been studied instead, the results may have been different.
- *Differences between field and laboratory exposure.* In field conditions the temperature of the seawater was the main influencing factor and the salinity did only have subordinate effect. However in laboratory conditions the situation was the opposite, where the salinity was found to

be the main influencing factor. The reason for this difference is not fully known, but it is assumed that it is caused by differences in the exposure conditions, e.g. pH of the exposure water.

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