Third RILEM workshop on Testing and Modelling the Chloride Ingress into Concrete
9-10 September 2002, Madrid, Spain

CONCEPTS IN CHLORIDE INGRESS MODELLING

Lars-Olof Nilsson

Dept. of Building Materials, Chalmers University of Technology, SE-412 96 Göteborg, Sweden.
From January 2003: Div. of Building Materials, Lund Institute of Technology, University of Lund, P O Box 118, SE-221 00 Lund, Sweden

Abstract

A brief summary is given on the present state-of-the art in modelling chloride ingress into concrete. Various concepts are defined and discussed, especially divided into concepts in the two types of models, physical and empirical models. A number of concepts where understanding still is lacking are pointed out and exemplified. Finally a number of questions are raised on how to proceed in further developing chloride ingress models.

1. INTRODUCTION

The “state-of-the-art” in modelling chloride ingress into concrete was tested at a Nordic (& *fib* TG) seminar in May 2001. A test case was defined with a given concrete, with given properties in a given environment. Exposure data up to 2 years in that environment was given. From that data it was easy to determine a suitable surface chloride content in that particular environment for the submerged zone.

Significant scatter was found in predictions of further ingress, by the “best” prediction models available, cf. Figure 1, even for the submerged zone. For the splash zone the scatter was fantastic. These results clearly show that we still have a long way to go before chloride ingress modelling is accurate enough for design applications.

An analysis of the predictions shows that the differences may very well be explained by the background exposure data for each prediction model. That data is more or less individual for each model. Better data and better exchange of data would probably reduce the scatter significantly. That exercise remains to be done!

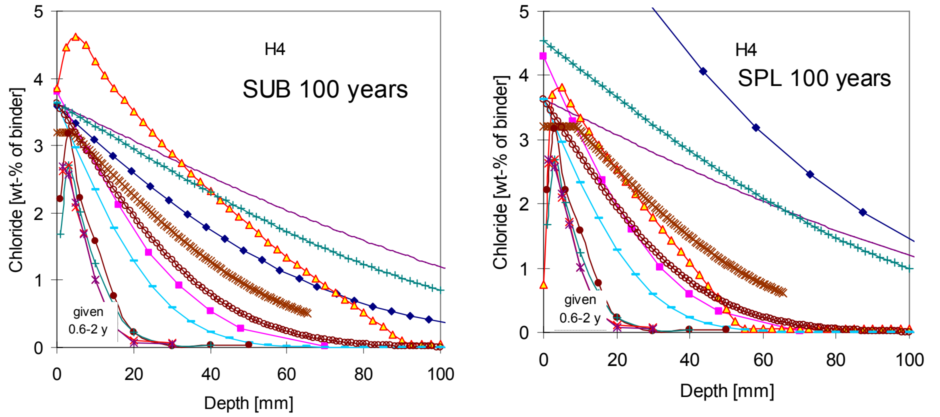


Fig. 1 Predicted chloride profiles from various prediction models for a given concrete in a well-defined environment and with profiles up to two years given. Prediction results for 100 years in the submerged (left) and splash zone.

A model for predicting chloride ingress into concrete always aims at predicting the chloride profile *C(x,t)* or at least the chloride content at the depth of the reinforcement. The output is always meant to be compared to a “critical chloride content that is relevant for reinforcement corrosion, see Figure 2! In recent models the prediction and the comparison should include some measure of the uncertainty in the prediction.

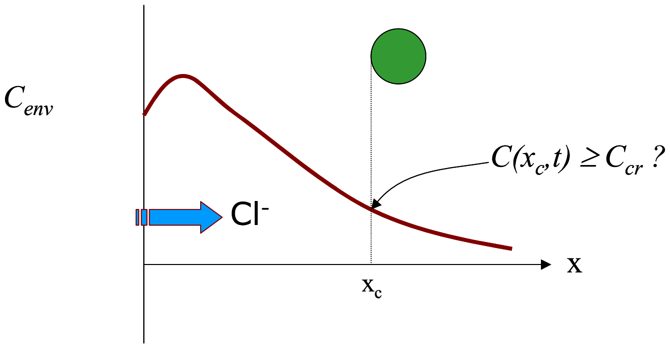


Fig. 2 The comparison between a predicted chloride content at the depth of the reinforcement and the chloride threshold level for corrosion

What is a “model”? A model has some input data that includes some information on concrete and some information on the environment. A model is the process of how to arrive into a predicted chloride profile or chloride content, from that input data. The output should then fit or explain data from field performance in various environments such as submerged, tidal/splash, atmospheric, wicking (tunnels, caissons), de-icing (roads, road bridges, parking decks, stairs), pools etc.

This is not yet possible for most of these cases, not only because the models are not yet good enough. A major reason is also the lack of very good data, including duplicates and data on the scatter. Also very little data from the submerged zone exists that could be used as reference for prediction models in that zone where the boundary conditions are well defined.

There are two types of models, in principle: "physical" and "empirical". For each type of model concepts on chloride transport, chloride binding/interaction and boundary conditions are discussed here. At the end a number of questions to discuss are pointed out.

2. "PHYSICAL" MODELS

In "physical models" all physical and (electro)chemical processes are described as scientifically correct as possible. True physical models use independently determined input data and no curve fitting to exposure data. Instead, field exposure data is used to validate predictions. If the comparison between predicted results and exposure data is not good enough, the model must be improved, or better data must be determined.

Sophisticated physical prediction models for chloride ingress into concrete contains at least two mass balances, and several relations, for chloride and for water, see Figure 3.

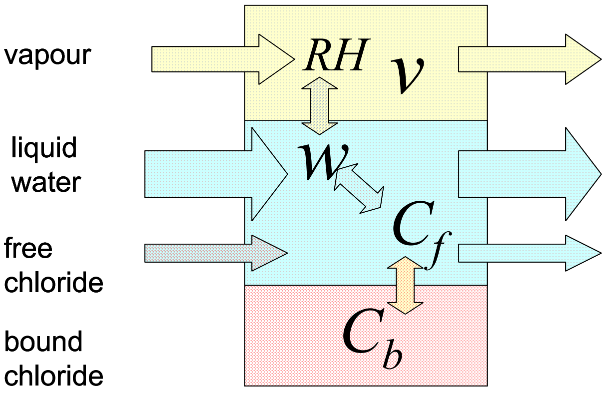


Fig. 3 The mass balance and interaction of chloride and water, in different phases.

The decisive concepts in physical models are concepts in chloride transport and in chloride binding.

2.1 Chloride transport concepts

Traditionally, Fick's 1st law has been used to describe the chloride flux as a result of pure diffusion in liquid water, with the concentration *c* of dissolved chloride as the transport potential.

$$q_{Cl} = -D_{F1} \frac{dc}{dx} \tag{1}$$

The "diffusion coefficient" is then defined by equation (1) and by the test set-up used to measure it. Nowadays it is widely recognized that Fick's 1st law is a very strong over-simplification of chloride transport. Instead, the effect of the electric potential field, from other ions and from an applied potential difference in migration tests, is included in the flux equation. The flux is then described by the Nernst-Planck equation.

$$q_{Cl} = -D_i \left(\frac{dc_i}{dx} + c_i \frac{d \ln a_i}{dx} + \frac{z_i F}{RT} c_i \frac{dV}{dx} \right) \tag{2}$$

For unsaturated flow a convection term is added

$$q_{Cl} = -D_i(w) \left(\frac{dc_i}{dx} + c_i \frac{d \ln a_i}{dx} + \frac{z_i F}{RT} c_i \frac{dV}{dx} \right) + c_i \cdot q_l \tag{3}$$

The "diffusion coefficient" in Fick's 1st law D_{F1} is obviously not a material property but depends on the conditions. Consequently, it cannot be determined by a simple "diffusion" test. Any attempt with straight forward diffusion cells will determine something else since equation (1) is not a correct description of what happens in such a test.

Instead it must be acknowledged that the flux of chloride is influenced by the other ions. In any test set-up for determining the "diffusion coefficient" D_i for chloride, using equation (2), the result will depend on the diffusion coefficients for all other ions. Consequently, it is not possible to determine the chloride diffusion coefficient directly in one simple test. Different approaches to solve this problem have been used. Truc (2000) made estimations from chloride migration tests where the diffusion coefficients for sodium, hydroxyl and potassium ions were adjusted to fit predictions from a multi-species model. Samsom (1999) instead utilized the diffusion coefficients for several ions from data for diffusion in a solution. By determining the "formation factor", i.e. the effect of the tortuosity and the restrictivity of the pore system, he could describe the flux of all ions by applying the same formation factor to the flux of all ions.

Required input parameters for chloride transport in physical models are several. The diffusion coefficients should be described at least as functions of temperature, moisture content, degree of hydration, depth from the surface etc. The description of the convection term in equation (3) requires the liquid water flow to be described.

Chloride and moisture transport in submerged HPC concrete HPC do not occur at saturated conditions, see Figure 4.

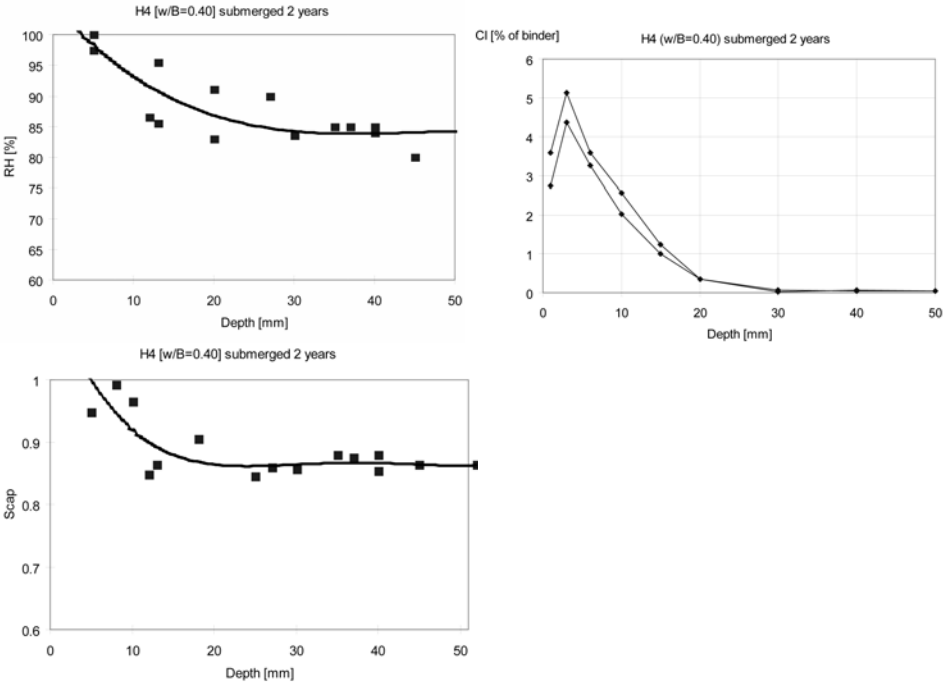


Fig. 4 Moisture profiles (left) and chloride profile (right) after 2 years of marine exposure, SRPC concrete, w/B=0.40, 5%Si

Moisture is obviously important for chloride transport! In Figure 4 the depths of penetration of moisture and chloride are about the same. Further ingress of chloride should be coupled to further ingress of moisture. It is not only a question of pure diffusion of chloride ions in pore water. The pore water may not be available even in submerged concrete!

2.2 Chloride binding/interaction concepts

The interaction between chloride and the matrix of cement-based materials is still not very well understood. Instead, for most applications a “binding isotherm” is used to give the relation between the free and bound chloride. Here a number of questions are still disputed, besides the approach by a binding isotherm at all. Since the binding isotherm I a pure empirical “property”, it must be measured and the effect of a number of parameters must be quantified.

The shape of the binding isotherm is one such question, cf. Figure 5. Does most of the binding really occur at concentrations close to zero, or is the chloride binding significantly concentration-dependent?

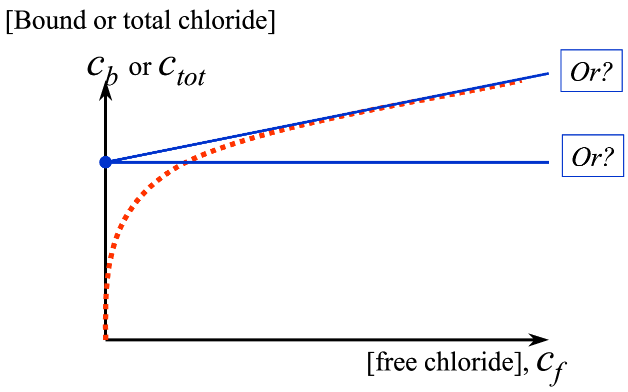


Fig. 5 Alternative shapes of a possible "binding isotherm".

Another important question is the relation between "free" and "bound" chloride, cf. Figure 6.

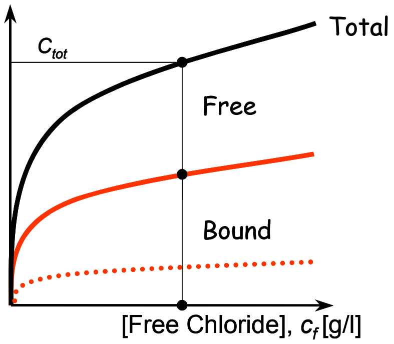


Fig. 6 The division of the total amount of chloride into "free" and "bound"

The question is of course how to define the concept "free" chloride! Several options are possible:

- *Free to move?*
- *Free to be leached out?*
- *Free to corrode steel?*
- *Free to be liberated?*

One important, but not obvious, question is whether the concentration of chloride in the pore water is equal to the concentration in the surrounding sea water or exposure solution. Some recent ideas on determining "free" chloride by leaching in water cause confusion about "free" and "water soluble" chloride that really question such a statement.

The answer to this question is absolutely vital for physical models, cf. Figure 7. Without consensus about this vital question, it is hardly possible to agree upon physical, or any, models at all.

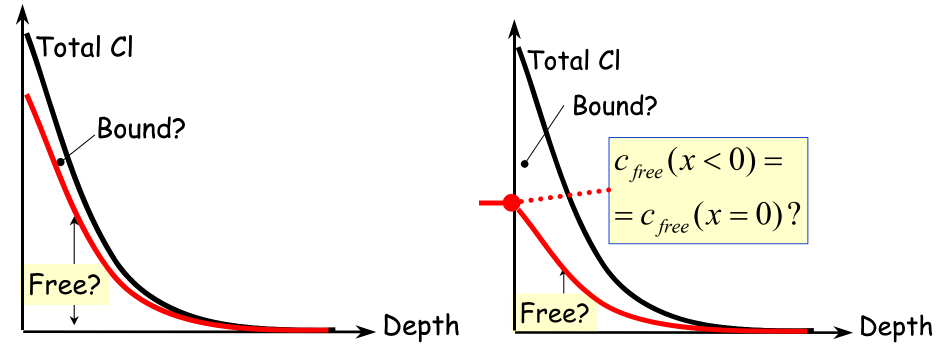


Fig. 7 Alternative divisions of the total amount of chloride into "free" and "bound" in a chloride ingress profile.

Chloride binding is, from measurements, a function of several parameters: concentration, pH, temperature, moisture content, gel content, type of binder, binder content, water-cement ratio, degree of hydration, time etc. The mechanisms behind all these observations are not fully understood and much more research is needed and measurements must be much better performed. See also Larsen (1998)!

Recently some "strange" time effects have been observed on chloride binding in submerged concrete. The surface chloride content has been found to be time-dependent $C_s(t)$! A longer exposure time does not only give deeper chloride ingress but also higher chloride content, cf. Figure 8.

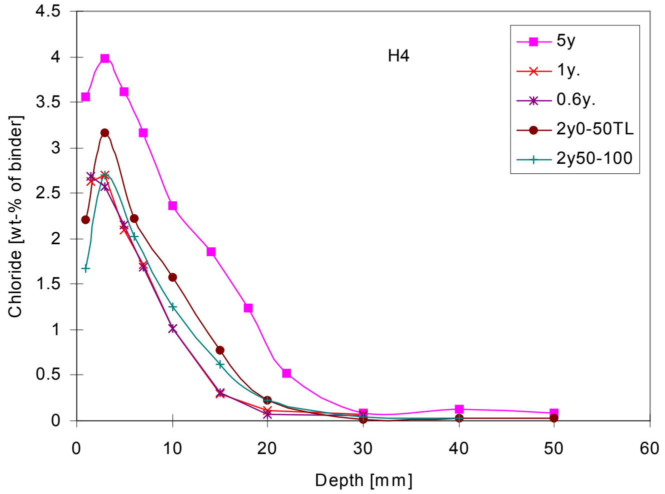


Fig. 8 Chloride profiles after several exposure times showing higher chloride concentration with time. Submerged SRPC concrete with w/b=0.40.

These observations cannot be explained by today's knowledge. The consequences of alternative causes and how these findings are utilized in chloride ingress models are quite contradictory, cf. Figure 9.

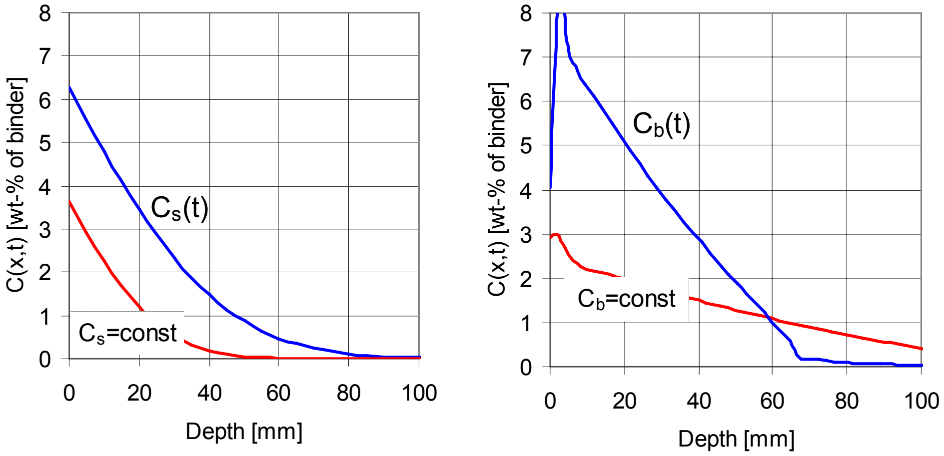


Fig. 9 The consequences of alternative causes for the findings in Figure 8: time-dependent surface chloride content $C_s(t)$ (left) or time-dependent chloride binding $C_b(t)$ (right).

A time effect on the "surface chloride content" C_s in an empirical ingress model, that has no simple explanation, has a significant consequence: a larger depth of penetration than with a constant C_s! On the contrary, a time effect on chloride binding will give a smaller predicted depth of penetration, simply because the larger chloride binding capacity with time will retard the ingress even more!

Conclusions on Chloride Binding in Physical Models:

- Binding has a significant retarding effect on chloride penetration,
- The shape of the chloride binding isotherm decides the shape of chloride profiles,
- "Free" chloride must be clearly defined and the definition agreed upon,
- Chloride binding data must be properly quantified; test method(s) required!
- Chloride binding test methods: keep other conditions stable!

3. "EMPIRICAL" MODELS

Empirical prediction models for chloride ingress into concrete utilize experience to fit data to mathematical models. If the fit is not good enough, more regression parameters are added! New experience is required for a new concrete or a new environment.

Predictions by empirical models should be done during the observation period only! Verification is then achieved from a comparison between data and model, cf. Fig. 10. Scatter between observations and predictions give the model uncertainty!

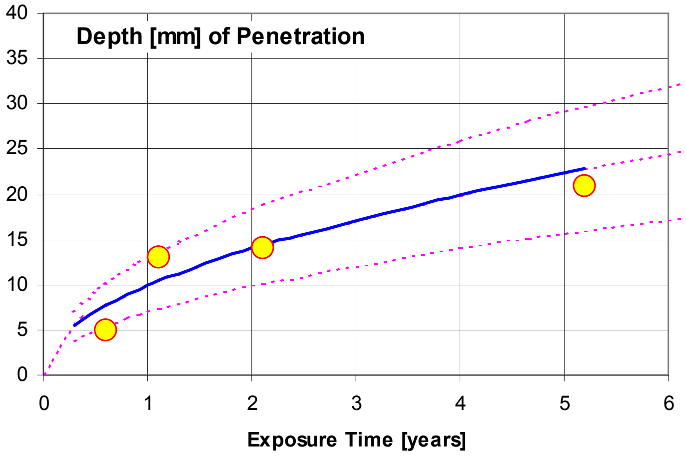


Fig. 10 Predicted chloride ingress by an empirical model in the time interval where the model is valid: the observation period!

Predictions beyond the data are highly questionable, since an empirical model by definition only is a mathematical fit to observation. Since it really has no clear physical meaning, it is dangerous to use it for extrapolation outside the borders of the observation data. Figure 11 shows this danger very clear. It is an alternative way of showing the predictions in the left part of Figure 1.

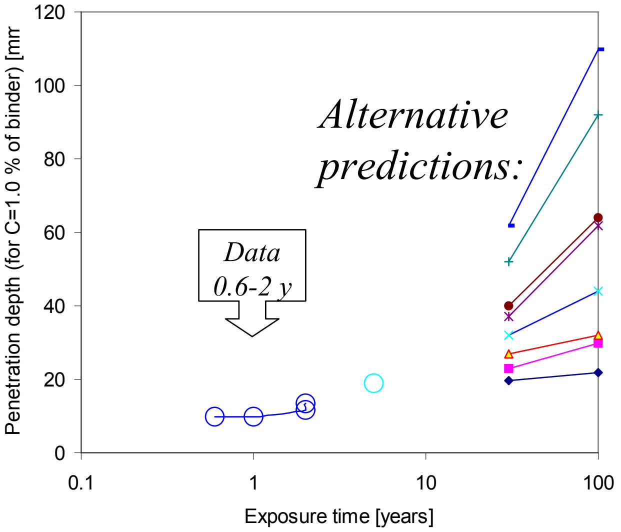


Fig. 11 The alternative predictions for 30-100 years in Figure compared to the observation data between 0.6 and 2 years. The circle at 5 years represents later measurements that were not available for the predictions.

3.1 Error-function models

The most frequently used empirical model for chloride ingress is the error-function solution to Fick's 2nd law. This model was almost the only one for twenty years, between 1970, when Collepardi proposed it, up to around 1990. In full it reads

$$C(x,t) = C_i + (C_{sa} - C_i)\,\mathrm{erfc}\,\frac{x}{\sqrt{4(t-t_{ex})\,D_a}} \tag{4}$$

but it is generally shortened to, if the initial chloride content is negligible

$$C(x,t) = C_{sa} \cdot erfc\left(\frac{x}{2\sqrt{D_a \cdot t}}\right) \tag{5}$$

The model has two regression parameters: D_a and C_{sa}. Both of them are regarded as being constants. D_a is called "diffusion coefficient", but in fact it only is a regression parameter.

An alternative empirical model that has been proposed is:

$$x_{c=C_{cr}} = k \cdot \sqrt{D_a \cdot t} \tag{6}$$

It looks much simpler, but it is not! The parameter *k* can easily be found from equation (5), where it is obvious that the two models really are identical!

3.2 Actual chloride transport concept

The error-function ERFC(*D, C_s, x, t*) is a mathematical solution to "Fick's 2nd law for : *C*(x=0, t)=C_s *C*(x, t=0)=0, *D*=const.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{7}$$

Fick's 2nd law looks like a mass-balance equation, and it really is. Rearranging equation (7) one gets

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}\left(- D \frac{\partial C}{\partial x} \right) \tag{8}$$

where the expression in parentheses is the flux. Additionally a mass-balance must describe the total amount of substance, i.e. the chloride content *C* in equation (8) must be the total amount of chloride c_{tot}. The equation (8) will then be:

$$\frac{\partial c_{tot}}{\partial t} = -\frac{\partial}{\partial x} q_{Cl} \tag{9}$$

Consequently, by comparing equations (8) and (9) it is obvious that the flux of chloride is described by:

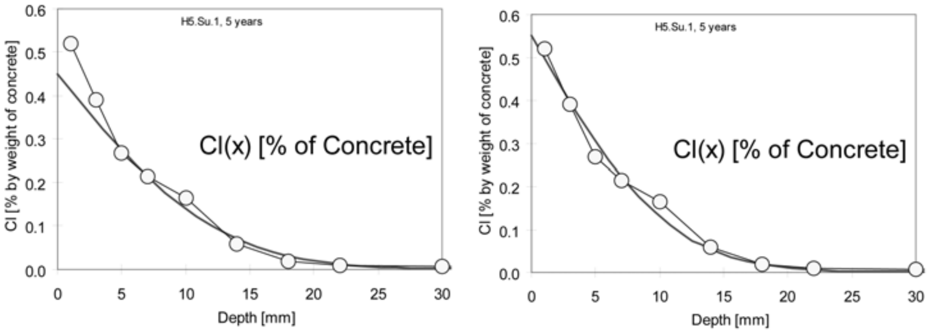
$$q_{Cl} = -D \frac{\partial c_{tot}}{\partial x} \tag{10}$$

The Fick's 2nd law used for chloride ingress into concrete utilizes the total amount of chloride c_{tot} as the flow potential!

3.3 Curve fitting

The regression parameters in empirical models are usually found from curve fitting observed ingress data with the error-function. No clear standard exists on how to perform the curve fitting. In some cases a selected number of data points close to the exposed surface are excluded, cf. Figure 12. Depending on the number of points and the quality of the data, two such fittings may give very different results. A standard procedure is needed and a clear way to give information on how the curve fitting was done must be developed.

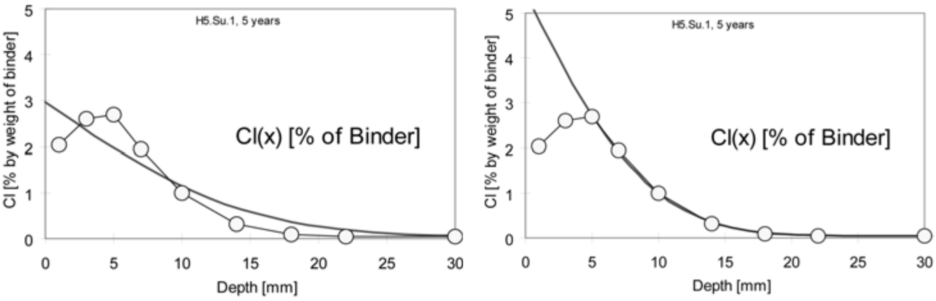
This is especially obvious when the data is expressed as chloride by weight of binder, cf. Figure 13. For concrete with large aggregate the binder content close to the exposed surface that was cast against formwork varies significantly, cf. Figure 14. The binder content is very high very close to the surface, which means that the chloride content by weight of sample is high, in spite of the chloride content per weight of binder is low, cf. Figures 12 and 13.



C_s=0.46%, D_{app}=2.85·10^{-13} m^2/s
Correlation = 0.994

C_s=0.55%, D_{app}=2.12·10^{-13} m^2/s
Correlation = 0.995

Fig. 12 Two examples of alternative curve fitting the same data



C_s=2.97%, D_{app}=4.04·10^{-13} m^2/s
Correlation= 0.94

C_s=5.45%, D_{app}=1.72·10^{-13} m^2/s
Correlation = 1.00!

Fig. 13 Two other examples of alternative curve fitting the same data as in Figure 12

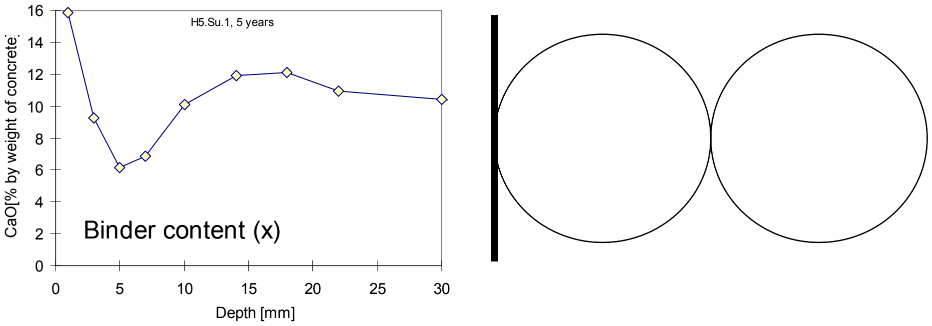


Fig. 14 The distribution of binder content in the concrete samples of Figures 12 and 13

The opposite is valid at a depth corresponding to half of the size of the large aggregate. That aggregate cannot come closer to the formwork, which means that there will be a higher “aggregate content” at that depth. A higher aggregate content means smaller binder content and, consequently, lower chloride content, if expressed a chloride by weight of sample. This is also visible in Figure 12!

Both of the two curve fittings in Figure 13 are doubtful and give very different results. The fitting in Figure 12 is not better, since that is done without taking into account that the data point have different binder contents but that is not accounted for in the empirical model!

The binder content is assumed constant in “all” empirical (and physical!) models. That means that we cannot expect that predicted chloride profiles can agree with profiles measured in concrete that was cast against formwork!

3.4 Time-dependent D

Empirical models in the beginning of the 1990’s were developed to include the effect that was obvious in data from different exposure times: a time-dependent D_{app}! Several researchers started to use expressions for the time-dependency like equation (11).

$$D_a = D_{aex}\left(\frac{t_{ex}}{t}\right)^{\alpha} \tag{11}$$

One example of data for 0.6 to 5 years of exposure is shown in Figure 15.

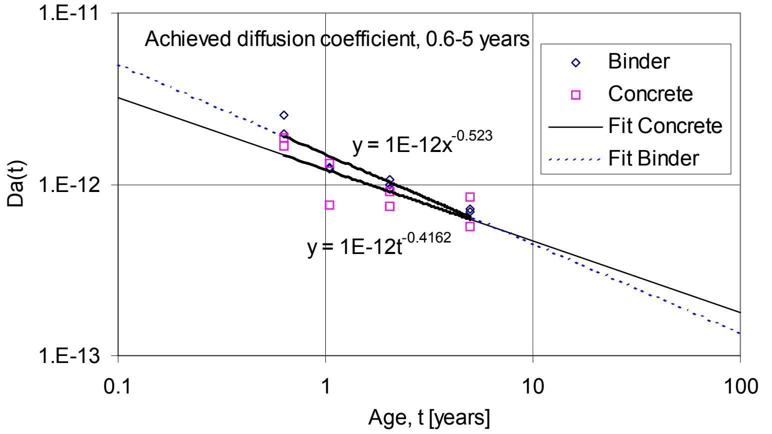


Fig. 15 Apparent "diffusion coefficients" plotted against the length of the exposure time

The time-dependency was found to be different in different exposure zones. Part of it could be explained by laboratory measurements showing a normal densification of concrete, somewhat different for different binders. The effect has not yet been fully explained. Can we use the observations for long-term predictions if we cannot understand it?

A time-dependent *D* causes a lot of confusion. On one hand there are observations showing the apparent *D* to be time dependent. That *D* is taken from curve fitting data after a certain length of exposure to the error-function. That means that the *D* is regarded as constant through the whole exposure and the *D* is a kind of an "average *D*" during that period, cf. Figure 16.

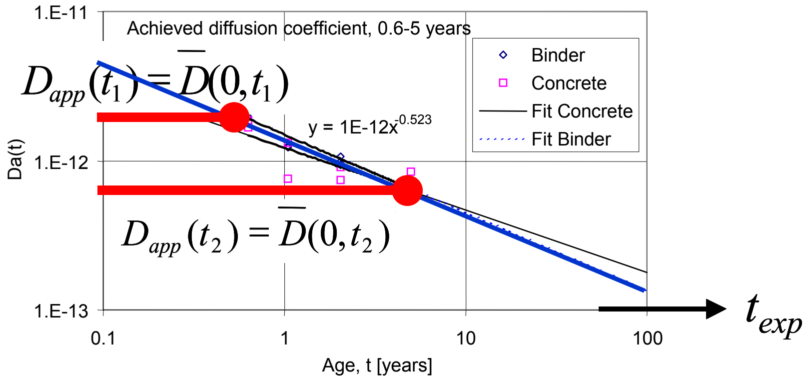


Fig. 16 The time-dependent apparent *D* after several lengths of exposure during which the *D* is assumed constant!

The time-dependency of the constant, apparent *D* during an exposure from 0 to t must not be confused with the diffusion coefficient at a certain age t.

$$\overline{D_{app}}(0,\underset{\boxed{t_{exp}}}{\underset{\uparrow}{t}}) \neq D_{test}(\underset{\boxed{age}}{\underset{\uparrow}{t}}) \qquad (12)$$

The time-dependency of the apparent diffusion coefficient must be explained before it can be used with confidence in predictions! Additionally, the age-dependency of a *D* being a material property must be determined. We need test methods for that!

4. BOUNDARY CONDITIONS CONCEPTS

Prediction models for chloride ingress are certainly not only a question of what happens inside the concrete. All prediction models rely heavily upon the relevance and the accuracy of the boundary conditions. Much more effort should be spent on quantifying the boundary conditions in various environments, and adjusted to different models. Some important concepts are discussed here.

4.1 Boundary conditions concepts in empirical models

In empirical models the boundary condition is expressed as a surface chloride content C_s, that really is the response by a particular concrete to particular environmental actions. That response does not only depend on the environment but also on the concrete! Consequently, a C_s cannot be taken as boundary conditions for a particular environment. The effect of the concrete must be considered as well.
The C_s is the total amount of chloride in the surface-near region of the concrete. Consequently, it depends on the porosity of the concrete and on the binding capacity of the concrete. That explains why C_s is a function of the concrete mix, especially the type of binder, the binder content, and the water-binder ratio. It also explains why C_s is a function of temperature, pH, carbonation etc.

Since the apparent diffusion coefficient obviously depends on the binding capacity, cf. equations (1) and (10), there is a correlation between the D_{app} and C_s for a particular concrete. They cannot be chosen independently!

In the 1990's the C_s has been regarded as time-dependent by a number of researchers. The explanation for this is not yet given, but in some environments it is obvious that the chloride content could increase with time, e.g. the splash zone in road environments. Drying and wetting in the splash zone of marine structures could possible explain a time-dependent C_s in that zone.

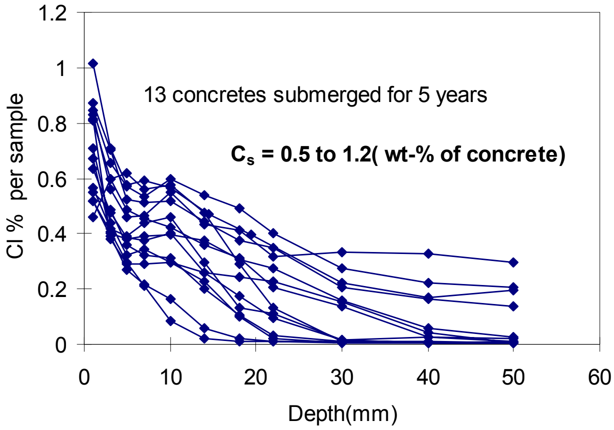


Fig. 17 Several examples of C_s = f(concrete mix) in one marine, submerged environment

However, recently it was observed that $C_s(t)$ also is time-dependent in the submerged zone of marine structures, cf. Figure 8. The effect was not visible if the data is expressed as chloride by weight of sample simply because of the large scatter, cf. Figure 18.

However, the time-dependency is clearly visible, if C_s is expressed by weight of binder, see Figure 19! We cannot explain why, however! This is vital, both for empirical models and for physical models.

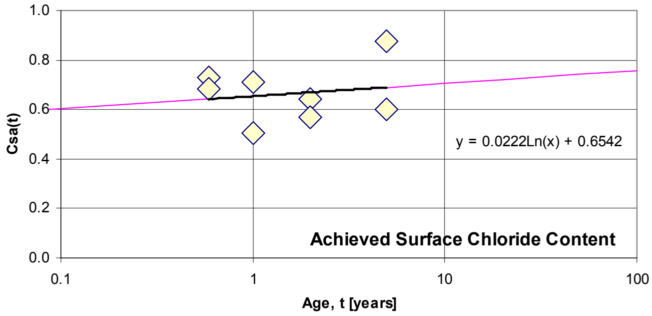


Fig. 18 Surface chloride contents C_s as a function of exposure times 0.6 to 5 years for the concrete in Figure 12. C_s expressed by weight of sample.

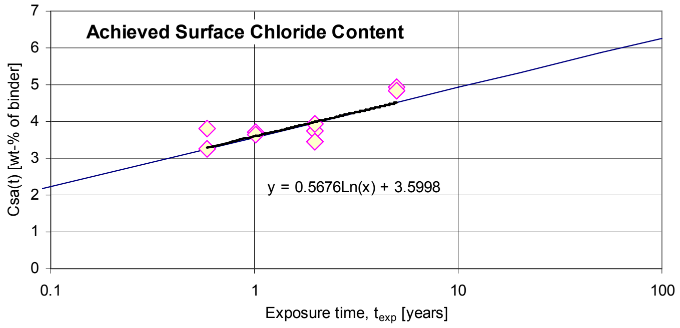


Fig. 19 Surface chloride contents C_s as a function of exposure times 0.6 to 5 years for the concrete in Figure 12. C_s expressed by weight of binder.

4.2 Boundary conditions concepts in physical models

The description of boundary conditions in physical models are much more complicated, since these models require boundary conditions in terms of chloride, temperature, humidity conditions at the very surface of the concrete: *C(x=0, t), W(x=0, t), T(x=0,t)*.

An obvious question is: Whose "responsibility"? Material researchers that develop sophisticated physical models will find no use of them if quantitative boundary conditions are not available. For the submerged zone of marine structures it is fairly simple, but for all other environments it is extremely complicated. The surface conditions at a particular concrete surface must be regarded as dependent on the location, orientation, distance, time etc.

We have very little data where the same concrete was exposed in two locations! Every researcher has been exposing his concretes in his own "back yard" with no possibilities to compare data with another researcher. Additionally we usually miss proper documentation of the exposure environment! A "splash zone" is not equal to a "splash zone" somewhere else!

A possible approach to make information on boundary conditions for physical models available in the future is to describe the environmental actions in steps from meteorological data up to the surface:

- Regional Climate
- Local Climate
- Location of the structure
- Distance from the source of chloride to the concrete surface
- Orientation of the surface

This approach has been analysed for the road environmental actions, cf. Figure 20. On the regional scale the macro climatic actions are the ones without a road at all! On the meso scale, the environmental actions are the one from the road surface, without even considering the presence of a concrete structure! At the micro scale the effect of the location, the size and the shape of the concrete structure is considered to give the actual environmental actions at a particular concrete surface.

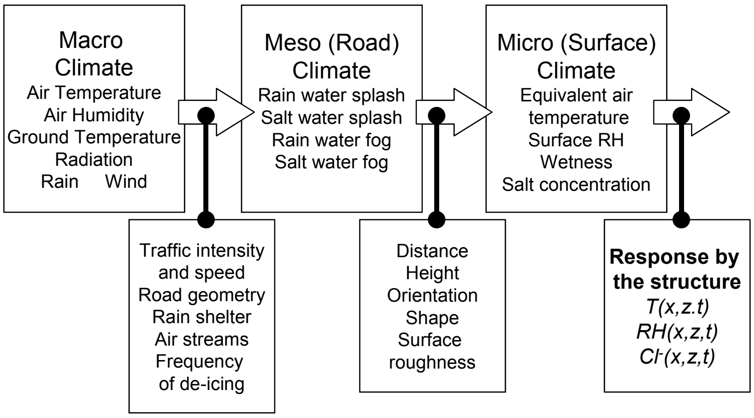


Fig. 20 An approach to stepwise quantify the environmental actions at a concrete surface in a road environment, starting from meteorological data.

Without the proper boundary conditions available, we are limited to observations of the response by concrete in various environments and during various conditions. We do have some information on the comparison between marine and road climates, cf. Figure 21.

The build-up of chloride profiles during one season is shown in Figure 22 for the same concrete as in Figure 21 (bottom). The two figures show the response by the vertical and horizontal surfaces respectively.

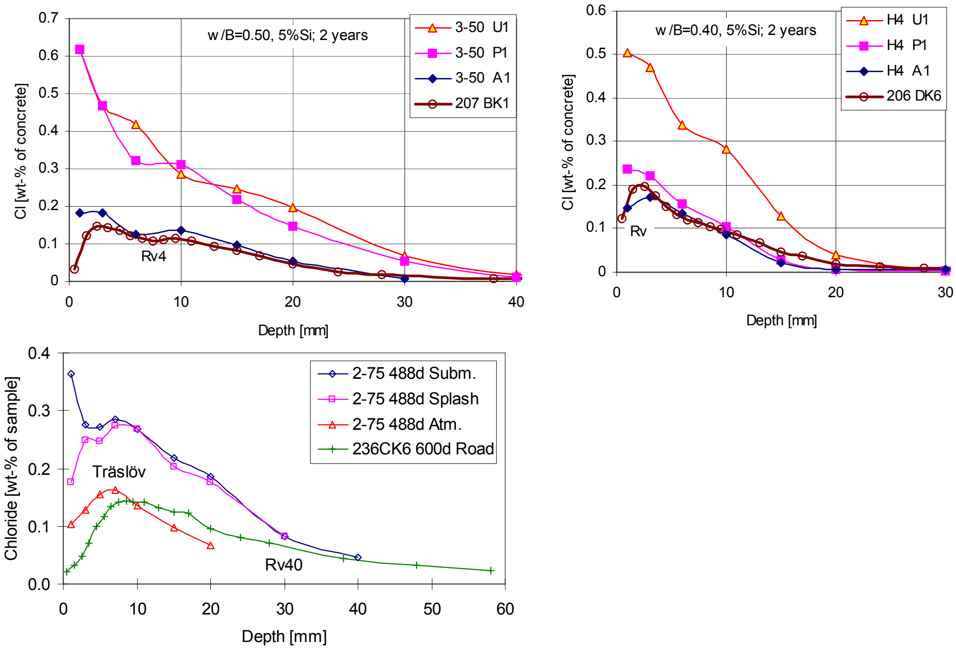


Figure 21. Chloride profiles for a SRPC concrete with w/b of 0.50 (top left), 0.40 (top right) and 0.75 (bottom) exposed to various chloride environments, a marine submerged (upper curves) and atmospheric and road environment (lower curves).

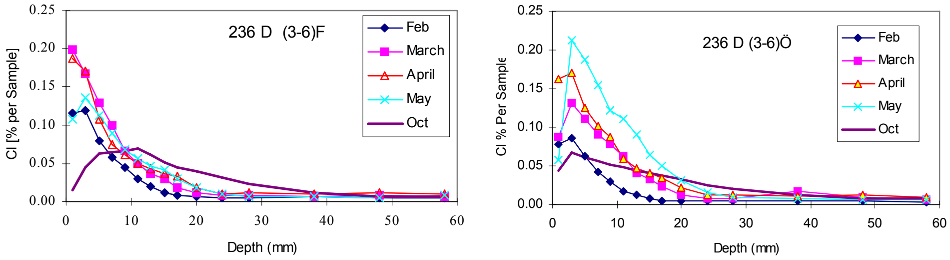


Figure 22. Chloride build-up and washout during the first winter and summer of the vertical (left) and horizontal (right) surface of a concrete with w/c=0.75 in a road climate.

Even though the chloride profiles have a certain uncertainty, some ±20 % /1/, which makes comparisons difficult, some indications could be pointed out. Some differences are clearly larger than the uncertainty. During the winter the chloride content in the surface near region is very large. The build-up seems to be more rapid for the vertical surface, but later during the winter, the horizontal surface gets a larger depth of penetration. This could be due to a longer time-of-wetness for horizontal surfaces, promoting the diffusion and convection of chloride further into the concrete. On the other hand, the wash-out is also more significant for the horizontal surface, more or less for the same reason. After the first winter and summer the chloride profiles are similar for the two orientations, in spite of the differences during the previous winter.

In the future, that kind of processes must be described if we want to use physical prediction models for complicated environments. For the time being, these difficulties favour the use of empirical models, because of the simple description of the boundary conditions, a C_s-value. That C_s for every individual concrete could be translated into an "equivalent" chloride concentration at the concrete surface. Then that could be used as boundary conditions for a new concrete, without having to perform an exposure program.

4.3 Conclusions on boundary conditions for road and marine environments

- The required surface climatic conditions are complicated to model,
- Physical models need quantification of a number of material parameters and a number of environmental parameters,
- The meaning of regression parameters in empirical models is not always easy to understand.
- Empirical models need huge data bases: a C_s for every concrete X, every road Y and every "water" Z!

5. QUESTIONS TO DISCUSS

Questions on "Concepts" in modelling chloride ingress into concrete are many. These are proposed to be dealt with in the workshop:

Physical Models
How far can/should we go?
What are the main obstacles?

Empirical Models
Do we dare to predict beyond data?
What main improvements are needed?

Models for Chloride Transport & Binding
What is lack of understanding?
What is lack of tools?

Models for environmental actions/boundary conditions
How to proceed?
How to cooperate?