

# Chloride profiles with a peak – why and what are the consequences for predictions?

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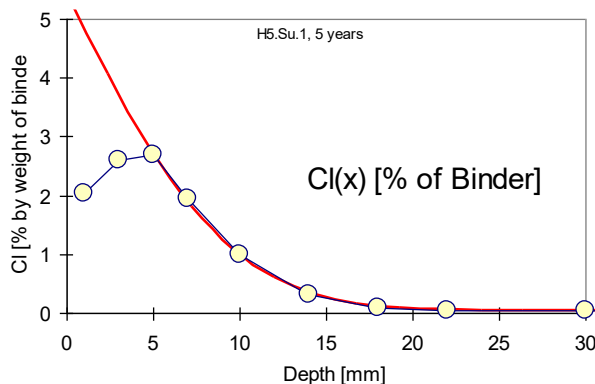
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**Abstract.** Chloride ingress profiles do almost always have a peak at some depth but most prediction models are missing this peak. Some prediction models, such as the *fib* model, simply “cut off” a slice of the concrete up to the peak in further predictions. Other prediction models use data only from the profiles beyond the peak but include the concrete up to the peak as if it has the same properties as the rest of the concrete. A physical model has been developed to quantify the local changes because of leaching and the consequences of these changes with time. The model uses Fick’s 1<sup>st</sup> law for chloride diffusion and linear chloride binding. The depth of leaching with time is modelled with a simple square-root equation. The consequences of leaching are assumed to be linear from the surface into the maximum depth of leaching. The consequences of leaching are modelled as depth-dependent changes of porosity, chloride binding and the diffusion coefficient in Fick’s first law.

## 1 Introduction

Almost all models for predicting chloride ingress into concrete are based on data from curve-fitting measured chloride profiles to solutions to Fick’s 2<sup>nd</sup> law of diffusion, especially the *erfc*-solution for semi-infinite cases with constant surface chloride content [1]. The curve-fitting gives two parameters, the apparent chloride diffusivity  $D_a$  and the apparent surface chloride content  $C_{sa}$ . An example is shown in figure 1.



**Fig. 1.** An example of a chloride profile for an SRPC-concrete with 5 % silica fume and a water-binder-ratio  $w/b$  of 0.25 after five years of exposure submerged in seawater: data from [2]. Two data points are excluded from the curve-fitting. The apparent surface chloride content  $C_{sa}$  is 5.5 % and the apparent diffusivity  $D_a$  is  $1.7 \cdot 10^{-13} \text{ m}^2/\text{s}$ . The correlation coefficient is 1.0.

When performing curve-fitting of a chloride profile several data points close to the surface are not included, cf. figure 1. The number of points to be excluded may be

selected by the individual that performs the curve-fitting, not always giving information on which points were excluded. It is common to exclude all points including, or excluding, the point at the top of the peak, to get as good fit as possible. The apparent surface chloride content  $C_{sa}$  frequently reaches an unreasonably high level when curve-fitting is performed in this way. This level has very little to do with the actual chloride content in the concrete.

A possible way of handling chloride profiles with a peak was demonstrated by Andrade et al [3]. The concrete is to be “rescaled” in such a way that the depth “0” is calculated from the depth of the top of the peak. A new “surface chloride content”, “ $C_{max}$ ”, is derived by curve-fitting to the data beyond the peak. This approach is what is used in the *fib* model for predicting chloride ingress [4], where the depth scale is rescaled by reduction of the depth-scale with the depth  $\Delta x$  of the peak. A slice of concrete with a thickness of  $\Delta x$  is neglected. Such an approach should over-estimate chloride ingress.

Alternatively, using data from curve-fitting to chloride data beyond the peak only, for predictions without excluding the slice of concrete between the surface and the peak, means that the concrete in this part is assumed to have the same properties as the rest of the concrete. Such an approach should under-estimate chloride ingress.

A few physical chloride ingress models include the effect of leaching in various ways. For instance, the original *ClinConc* model [5] included leaching of alkalis and had a pH-dependent, non-linear chloride binding. The pH-dependency of binding did not give any peak but changed the curvature of the predicted profiles.

Models that include temperature-dependency of binding, however, could predict temporary peaks in total

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chloride profiles each summer [6]. Since samples from submerged concrete preferably are taken in summertime, these are the profiles we mostly get, with a peak that partly is due to the temperature when profiling.

Several models describing ion transport in cementitious materials include the chemical interactions between the ions in the pore solution, sea water and the binder reactions products. A few very sophisticated models so far [7] include many of the consequences of leaching on chloride binding and chloride transport properties. The codes, however, are not open for public use which means that it is not quite clear exactly what and how various parts are included. Comparison between these models, and between such models and more simple empirical models, are rare [1].

The surface region of concrete, where these peaks occur, are not homogeneous. The binder content varies a lot because of the “wall effect” [8]. Close to a cast concrete surface large aggregate particles are lacking, creating a very large binder content. On the contrary, at a depth corresponding to half the size of the largest aggregate particles, these aggregate particles are over-represented, causing a very low binder content. No chloride ingress model, to the author’s knowledge, is considering the distribution of binder next to the surface and its consequences on chloride binding.

## 2 Consequences of leaching

The main reason for occurrence of the peak in chloride profiles in concrete submerged in seawater seems to be leaching that affects the surface region of concrete in various ways. Leaching of alkalis changes the pH in the pore solution that will change chloride binding. Leaching of Portlandite will eventually create large voids in the pore system and change the tortuosity and the constrictivity. Leaching of CSH and other binder reaction products will reduce chloride binding, increase the porosity and change the microstructure.

Recently, a number of these parameters were quantified by Fjendbo et al [9] for several concretes. Their studies inspired the development of a model for chloride ingress that includes the effects of leaching.

## 3 The model

A simplified physical model for chloride ingress, using finite differences, has been developed to quantify the local changes due to leaching and the consequences of these changes with time. The model uses Fick’s 1<sup>st</sup> law for chloride diffusion and linear chloride binding. The depth  $X_L$  of leaching with time is modelled with a simple square-root expression,  $X_L = k_L \cdot \sqrt{t}$ .

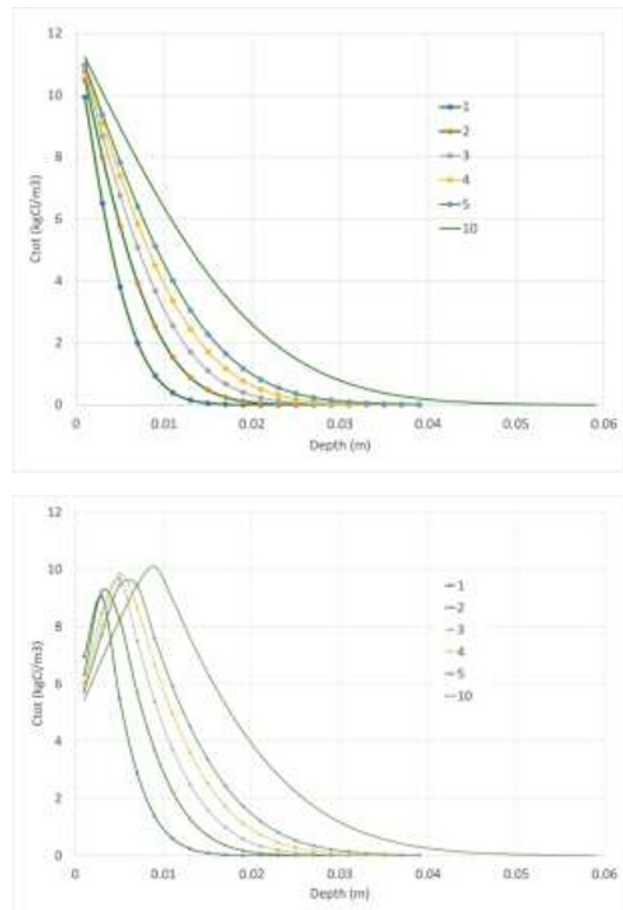
The consequences of leaching are assumed to be linear from the surface into the depth of leaching. The consequences of leaching are modelled as depth-dependent changes of porosity,  $p$ , chloride binding capacity,  $dc_b/dc_f$ , and the diffusion coefficient  $D_{F1}$  in Fick’s first law.

An example of chloride profiles from the model is shown in figure 2, without and with leaching included.

The input parameters for figure 2, partly estimated from [9], are:

- Binder content  $B = 360$  (90)  $\text{kg/m}^3$ .
- Diffusion coefficient  $D_{F1} = 0.5 \cdot 10^{-12}$  ( $1 \cdot 10^{-11}$ )  $\text{m}^2/\text{s}$ .
- Chloride binding capacity  $dc_b/dc_f = 0.003$   $\text{kgCl/kgBinder}$  per  $\text{kgCl/m}^3\text{pores}$ .
- Porosity  $p = 0.1$  (0.2).
- Leaching coefficient  $k_L = 0.003$   $\text{m}/\sqrt{\text{year}}$ .

Parameter values in parenthesis are the ones at the concrete surface when leaching is included.



**Fig. 2.** Examples of predicted chloride profiles for 1-10 years exposure to seawater with  $[Cl]=10$  g/l, without (top) and with (bottom) leaching included.

The model, without leaching (top part of figure 2), gives perfect fits for all exposure times to the *erfc*-solution to Fick’s 2<sup>nd</sup> law with a diffusivity  $D_{F2}$  of [10]

$$D_{F2} = \frac{D_{F1}}{p \cdot \left( 1 + \frac{dc_b}{dc_f} \left[ \frac{\text{kg}}{\text{m}^3} \right] \right)} = \frac{D_{F1}}{p \cdot \left( 1 + \frac{dc_b}{dc_f} \left[ \frac{\text{kg}}{\text{kgB}} \cdot \frac{B}{\text{kg}} \right] \cdot \frac{B}{p} \right)}$$

$$= \frac{0.5 \cdot 10^{-12}}{0.1 \cdot \left( 1 + 0.003 \cdot \frac{360}{0.1} \right)}$$

$$= 4.2 \cdot 10^{-13} \text{m}^2/\text{s}$$

and a surface chloride content  $C_s$  of

$$\begin{aligned}
 C_s(x = 0) &= c_b(x = 0) + c_f(x = 0) \\
 &= 10 \cdot 0.003 \cdot 360 + 10 \cdot 0.1 \\
 &= 10.8 + 1.0 = 11.8 \text{ kgCl/m}^3
 \end{aligned}$$

These two parameters could be regarded as the true transport properties of this concrete, in those parts where no leaching has occurred.

#### 4 The position of the peak

The results from the model demonstrate the movement of the peak inwards with time, as also found in long-term chloride ingress data, e.g. [9][11], from submerged concretes.

The major parameter for the occurrence of a peak seems to be the loss of chloride binding, as seen from parameter analysis by the model. The changes of the porosity and the diffusion coefficient have minor effects on the shape of the chloride profiles and do not change the position of the peak.

#### 5 Neglecting the concrete up to the peak

The effect of neglecting the changes in material properties in the leached parts of the concrete is quantified by comparing predictions with these changes and predictions using the error-function solution to Fick's 2<sup>nd</sup> law with chloride diffusivities from curve-fitting the profiles predicted by the model.

The apparent diffusivity is the same,  $D_a = D_{F2} = 4.2 \cdot 10^{-13} \text{ m}^2/\text{s}$ , with and without leaching! The difference, however, is the apparent surface chloride content that is much higher with leaching included,  $C_{sa} = 18 \text{ kgCl/m}^3$ , compared to  $11.8 \text{ kgCl/m}^3$ , i.e. some 50 % higher.

Consequently, the effect of leaching can be handled by performing the traditional curve-fitting to the *erfc*-solution to Fick's 2<sup>nd</sup> law, and perhaps also to the Mejbropoulsen solution [1], and accept the usage of unnaturally large apparent surface chloride contents  $C_{sa}$ .

The effect of leaching, from what is seen with the model, is the same penetration depth but much higher chloride levels when leaching is considered. This is of course a consequence of the loss of binding, the increased porosity and the increase in diffusion coefficient in the leached part of the concrete. This part has a much smaller resistance to ingress of chlorides than the bulk concrete.

#### 6 The *fib* model

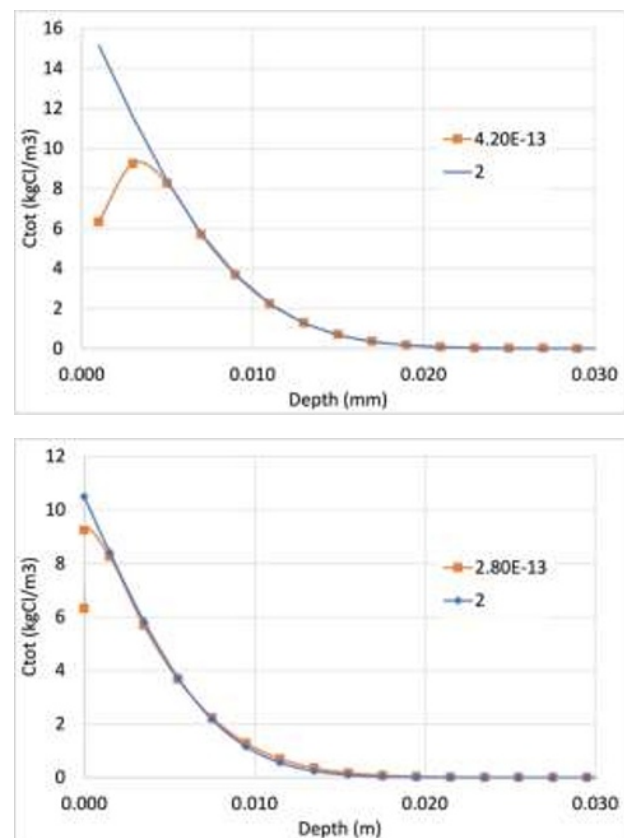
The effect of neglecting a slice of the concrete in the *fib* model has been quantified with the model by comparing predictions with and without this slice. The depth of the peak, as evaluated from the predicted profiles, is compared to the depth of leaching in Table I. The depth of the peak is somewhat uncertain because of the limited resolution in the finite-difference approach.

By "cutting off" a slice of concrete with the thickness equal to the depth of the peak, for each exposure time, curve-fitting the remaining chloride profile to the *erfc*-

solution gives apparent diffusivities and surface chloride contents. One example of the curve-fitting in the two cases is shown in figure 3 for an exposure time of two years.

**Table 1.** The depths of the peak  $\Delta X$  and the depths of leaching  $X_L$  for different exposure times.

Exposure time (years)	Depth of leaching $X_L$ (mm)	Depth of the peak $\Delta X$ (mm)
1	3.0	2.8
2	4.2	3.5
3	5.2	4.7
4	6.0	5.1
5	6.7	6.0
10	9.5	8.8

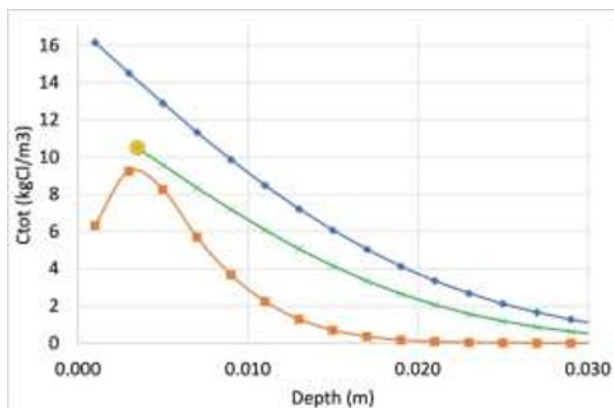


**Fig. 3.** Curve-fitting the *erfc*-solution to the full profile (top) and the profile (bottom) with  $\Delta X=3.5 \text{ mm}$  cut off

The apparent diffusivity  $D_a$  becomes only  $D_a = 2.8 \cdot 10^{-13} \text{ m}^2/\text{s}$  when the curve-fitting is done to the profile where a slice is cut off as in the *fib* model. The apparent surface chloride content  $C_{sa}$  becomes  $10.5 \text{ kgCl/m}^3$ . These two parameters are evaluated according to the principles in the *fib* model.

A comparison is made in figure 4 between the two alternative ways to make predictions from a profile after a short exposure time, here two years, up to an exposure for ten years. The surface chloride content  $C_{sa}$  in the *fib*

model is marked with a large green circle at a depth of  $\Delta X=3.5$  mm.



**Fig. 4.** Predictions by using the profile (orange, bottom curve) including leaching, after two years of exposure. Predictions are done for 10 years of exposure, with  $D_a$  and  $C_{sa}$  from traditional curve-fitting (blue, top curve) and with  $D_a$  and  $C_{sa}$  from the fib model with a slice cut off (green, middle curve)

The depths in the fib model, middle curve in figure 4, should be rescaled by subtracting  $\Delta X$  from the horizontal x-scale. Then the difference between the two approaches will be much larger.

## 7 Discussion and conclusions

Even though the model includes leaching in a very simple way the results look very much like the results by Fjendbo et al [9]. Their data for the leached zone has a low resolution; the numbers are averages over the whole thickness of the first sample from their concretes. To improve a model including leaching the distribution of the parameters within this thickness should be studied in more detail.

The diffusion coefficient  $D_{F1}$  at different depths in this outer layer could perhaps be quantified with a non-steady-state chloride migration test method where the electrical field is applied parallel to the concrete surface. It is not obvious, however, that the  $D_{F1}$  at a certain depth is the same parallel and perpendicular to the surface.

The results from the model seem promising. The model is very simple but could easily be improved and extended once better knowledge is available. It would be interesting to verify it against field data; data that is available but could not yet be used because of time-constraints.

More sophisticated models, that describe the chemical interactions in a more correct way, must also include the consequences of leaching. Input data for those consequences, however, are still missing to a large extent.

The results from applying the fib model are worrying. This model uses a fixed peak that does not move with time and it uses an apparent diffusivity that is much smaller than the actual diffusivity. The results implicate that this model severely under-estimate chloride ingress, in spite

of a slice being cut off. This must be analyzed in more detail.

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