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Combining Chloride Migration and Diffusion Tests to Estimate Freundlich Chloride Binding Parameters and Improve Predictions of Chloride Ingress

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ABSTRACT
Chloride binding plays a major role with respect to chloride ingress. On one hand, engineering models often rely on "apparent" diffusion coefficients, which account for both the diffusion of chlorides in the pore solution and chloride binding. On the other hand, mechanistic models intend to consider the two phenomena separately. However, the inputs to model chloride binding are quite complex to acquire, because they require dedicated experiments that are usually only conducted for research purposes.

In this paper, an approach is proposed to estimate binding parameters from chloride ingress profiles. First, the effective diffusion coefficient is measured with a chloride migration test. Then, a chloride profile from a diffusion test is fitted with a model where transport of free chlorides follows Fick's second law, and free and bound chlorides are linked by a Freundlich equation. Finally, the surface concentration and the Freundlich parameters are adjusted to obtain the best possible fit. The derived Freundlich parameters are fairly close to the ones measured in dedicated chloride binding experiments. A case study applying this approach to concrete elements exposed to seawater in a Danish harbour is also presented.

Key words: Chloride, diffusion, binding, modelling

1. INTRODUCTION

Chloride ingress is a great concern for reinforced concrete structures exposed to salt, due to the risk of chloride-induced corrosion of the rebars. For this reason, the design service life is often calculated based on chloride ingress predictions [1].

Two phenomena play a major role in chloride ingress:

1) *Diffusion*: Chloride ions diffuse from the exposed surface via the pore solution. A simple model to describe chloride diffusion is Fick's second law [2]. More complex models, based on the Poisson-Nernst-Planck equation [3], account for multi-species diffusion in the pore solution.
2) *Binding*: Cement hydrates, particularly AFm, C-S-H, and C-A-S-H, can bind chloride chemically or physically [4]. A common way to describe chloride binding is by the Freundlich

isotherm, which expresses a relationship between free and bound chlorides at a given temperature [5].

A simple engineering model consists in assuming that the total chloride content – equal to the sum of free and bound chlorides – follows Fick's second law. In this case, the diffusion coefficient is called "apparent", because it is a lumped parameter that characterises both the diffusion of free chlorides and chloride binding [6]. Such approach is represented by Equation (1), where c_t is the total chloride content, x is the depth from the surface, t the exposure duration, and D_{app} the apparent chloride diffusion coefficient.

$$\frac{\partial c_t}{\partial t} = D_{\text{app}} \frac{\partial^2 c_t}{\partial x^2} \tag{1}$$

The contribution of diffusion and binding can also be accounted for separately, via a mechanistic model. In this case, the free chloride content follows Fick's second law with an "effective" diffusion coefficient, D_{eff}. For this approach, there has to be a link between the free (c_f) and bound (c_b) chloride contents, and in this paper it is assumed that this link is represented by a Freundlich isotherm. This is shown in Equations (2a-2c), where α and β are empirical parameters, usually determined by curve fitting.

$$\frac{\partial c_f}{\partial t} = D_{\text{eff}} \frac{\partial^2 c_f}{\partial x^2} \tag{2a}$$

$$c_{\text{b}} = \alpha \cdot c_{\text{f}}^{\beta} \tag{2b}$$

$$c_t = c_f + c_b \tag{2c}$$

In previous studies, Jensen et al. [7,8] introduced a chloride ingress model based on Equations (2a-2c). The chloride profile is computed by discretising the governing equations, implying that the entire profile is calculated for each time step. Previous work [9] using Jensen's model showed that the difference between apparent and effective diffusion coefficients is significantly more pronounced for diffusion tests than for migration tests. Moreover, it was shown that the coefficients from migration tests correspond fairly well with the effective coefficient from diffusion tests. In other words, $D_{m,app} \approx D_{m,eff} \approx D_{d,eff,}$ where the subscripts m and d refer to migration and diffusion, respectively. This is illustrated in Figure 1, which shows that $D_{d,eff}$ determined after 4 weeks of curing + 8 weeks of chloride exposure falls in between D_m determined at the beginning and in the end of the diffusion experiment, both for the apparent and effective coefficient.

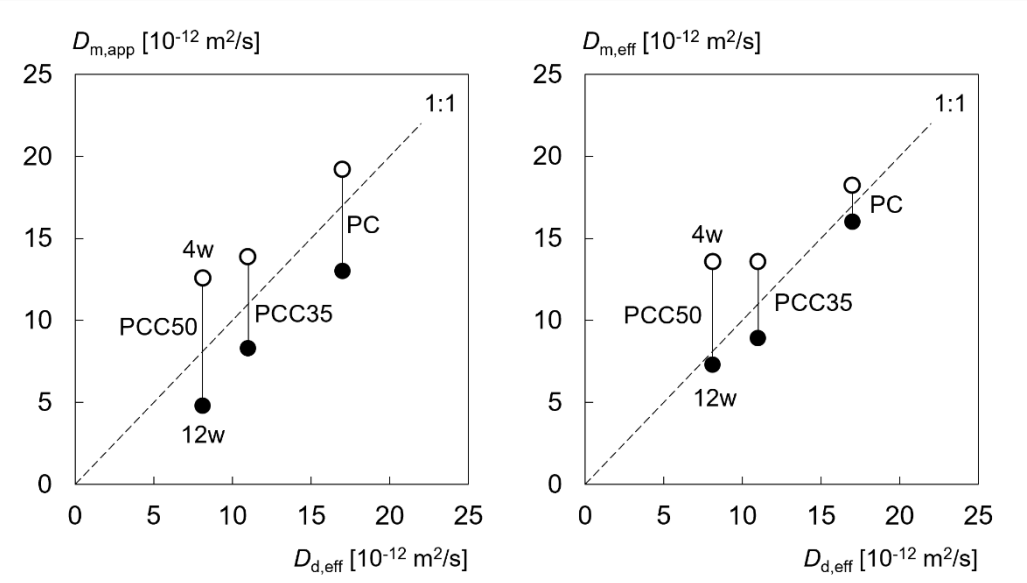

Figure 1 – $D_{d,eff}$ determined after 4 weeks of curing + 8 weeks of chloride exposure, and D_m determined at the beginning and in the end of the chloride exposure period [9]. Left: Apparent coefficient from migration test, $D_{m,app}$. Right: Effective coefficient, $D_{m,eff}$. The three sets of points correspond to different cementitious binders, identical to those in the present paper.

In summary, chloride binding is a crucial phenomenon to account for in chloride ingress modelling. However, determining chloride binding parameters requires complex and lengthy experiments, which are not routinely done in material testing, unlike migration and diffusion tests. Therefore, this paper addresses the following question: *Is it possible to derive information about the binding properties of a binder, without performing dedicated binding isotherm experiments?* To do so, the outcomes of migration and diffusion tests were combined with modelling using "Jensen's model". Experimental data published previously are used to illustrate the proposed analysis. Several chloride binding models have been proposed over the years, e.g., linear, Freundlich, Langmuir or Poisson-Nernst-Planck [3,10]. In this work, it was decided to select one model, namely Freundlich. However, the approach presented in this paper may be adapted to other chloride binding models. Finally, since the binder composition has a strong influence on the chloride binding isotherms [8,11], three binders were considered: A pure Portland cement, and two ternary blends with calcined smectitic clay and limestone. Subsequently, field data from a Danish marine exposure site are used as a case study.

2. MATERIALS AND METHODS

All laboratory work on paste samples is reported in detail in [9]. However, for the sake of completeness of the present paper, the main elements are summarized in the following. This allows understanding of the background of the data used for modelling.

2.1 Materials

A Portland cement (PC) and two Portland composite cements (PCC) manufactured from the same clinker were used. In PCCs, the clinker was substituted with a "low-grade" calcined smectitic clay (CC) and a limestone filler (LL) in the following proportions:

- PCC35: 65 wt.% PC, 17.5 wt.% CC, 17.5 wt.% LL
- PCC50: 50 wt.% PC, 33.3 wt.% CC, 16.7 wt.% LL.

Table 1 shows the chemical composition of the cements as determined by X-Ray Fluorescence (XRF) and Quantitative X-Ray Diffraction (QXRD). QXRD performed on PC gave the following mineralogical composition (wt.%): C_3S: 64, C_2S: 12, C_3A: 5 and C_4AF: 9. The composition of the reactive part of CC was derived from a mass balance calculation combining XRF and QXRD results, where the non-reacting crystalline phases were subtracted from the total amount of each compound. The non-reactive phases were quartz (SiO_2, 7.0 wt.%), hematite (Fe_2O_3, 0.6 wt.%), paragonite ($H_2NaAl_3Si_3O_{12}$, 2.0 wt.%) and rutile (TiO_2, 0.4 wt.%). Calcite ($CaCO_3$, 5.6 wt.%), Anhydrite ($CaSO_4$, 0.5 wt.%) and smectite ($H_4Al_4K_1O_{12}Si_2$, 6.1 wt.%) were also found by XRD but considered as reactive.

Table 1 – Chemical composition of the materials (in wt.%) measured by XRF. For CC, "Reactive" refers to the part of the material that is assumed to be available for reaction. It was calculated by subtracting the content of assumed inert crystalline phases (quartz, hematite, paragonite and rutile) from the total chemical composition.

Oxide	PC	CC		LL
		Total	Reactive	
SiO_2	19.2	49.0	41.2	2.0
Al_2O_3	5.2	17.3	14.8	0.4
Fe_2O_3	3.7	9.7	7.9	0.1
MgO	1.0	2.5	2.5	0.3
CaO	63.4	10.1	10.1	54.2
Na_2O	0.33	0.81	0.69	0.03
K_2O	0.38	2.66	0.56	0.06
TiO_2	0.2	1.0	0.0	< 0.1
P_2O_5	0.3	0.2	0.0	0.1
SO_3	3.1	1.0	1.0	0.1
LOI	3.2	4.9	4.9	42.5
Sum	100.1	99.7	83.7	100.0
d_{50} [µm]	14	16	-	4

Paste with *w/b* = 0.45 was prepared, paste cylinders (Ø22 mm, length approx. 110 mm) were cast, and they were sealed cured for 28 days at 20°C. Such *w/b* was chosen to obtain similar flow values for the different mixtures, while using reasonable amounts of superplasticizer (MasterGlenium SKY 851).

2.2 Methods

Migration

Chloride migration was performed according to a version of NT BUILD 492 [12] modified to test smaller paste specimens instead of the Ø100 mm concrete specimens assumed in the test standard. 50 mm long pieces of paste were cut and vacuum saturated with a saturated calcium hydroxide solution for 18 ± 1 h. Two specimens were tested together in the migration setup, and two setups ran in parallel. In the setup, each specimen had its own anolyte, 20 mℓ of a 0.3 M NaOH solution, and the two specimens in the same box shared the same catholyte, 7 ℓ of a 10 wt.% NaCl solution. Since paste samples were used, Appendix 2 in NT BUILD 492 [12] could not be used to choose the voltage and the test duration. Instead, results from a previous study using the same setup [13] were used to select appropriate settings to obtain a chloride penetration depth of around 25 mm during a 24 h migration period. The following voltages were applied: 14 V for PC and 30 V for PCC35 and PCC50.

After the migration period, the specimens were split longitudinally into two halves, and a 0.1 M $AgNO_3$ solution was sprayed onto the broken surfaces to identify the chloride penetration front. The average of two measurements was taken as the penetration depth.

Diffusion

After the 28 days of sealed curing, the approx. 110 mm long paste cylinders were first capillary saturated by immersion in a saturated calcium hydroxide solution for two days, which was sufficient to reach constant mass. Then, the paste cylinders were coated with epoxy resin on all sides and cured for another two days in room conditions. Subsequently, the cylinders were sawn through the middle to obtain two halves, each approx. 50 mm long. Four specimens, where the saw-cut surface was the only surface not coated by epoxy, were then placed in a plastic bottle containing 450 mℓ of a 10 wt.% NaCl solution, which was stored at 21 ± 2°C and gently shaken every week. To minimize leaching, the solution was not replaced during the test.

After approx. 8 and 26 weeks of exposure, total chloride profiles were made. Each specimen was sliced, starting from the chloride-exposed side: 0-2, 2-6, 6-10, 10-14, 14-18, 18-22, 22-26, and 26-30 mm. Each slice was crushed, oven-dried, digested in an HNO_3 solution, and titrated with an automatic potentiometric titrator using 0.1 M $AgNO_3$.

Binding

Cement pastes were cast with PC, PCC35 and PCC50 at *w/b* = 0.50, without superplasticizer. The *w/b* is different from the previous experiments because these samples were originally cast for

another purpose. The specimens were sealed cured for approx. 1.5 years at 20°C. The different *w/b* were accounted for during data analysis [9], therefore no significant impact on the interpretation is expected.

Care was taken to minimize leaching during chloride exposure through the following procedure. Paste specimens were crushed into pieces < 2 mm. Artificial pore solutions were prepared by submerging 120 g of crushed paste into 120 g of demineralised water, for 6 weeks. NaCl solutions were then prepared at concentrations of 0, 0.125, 0.25, 0.5, 1.0 and 2.0 mol/ℓ, using the artificial pore solutions as solvents. Then, 20 g of freshly crushed paste was mixed with 10 mℓ of such a NaCl solution for each concentration. The slurries were kept in plastic containers and stored at 20°C for 6 weeks, with regular shaking. Subsequently, the plastic containers were centrifuged at 4000 rpm for 2 min, and 0.5-1 mℓ of the supernatant was pipetted. Cl titration was done with an automated potentiometric titrator.

Field exposure

As part of a previous project ("Grøn Beton II", 2014-2019) [14], concrete elements (2 x 1 x 0.2 m) were cast and exposed to various conditions, i.e., outdoors close to a highway and submerged in two Danish harbours. The elements were placed in such a way that approx. 1 m is below the average waterline, and 1 m is above. Some pictures of the exposure site are shown in Figure 2.

Figure 2 – Field exposure site at Hirtshals. Left: overview. Right: Close-up on a concrete element.

Several mixes contained calcined clay, and one had a binder composition that resembled PCC35, with 30% PC substitution with a 1.5:1 mix of calcined clay and filler. The mix design is given in Table 2. The filler was a grey microfiller from Aalborg Portland. The grey microfiller comes from the bypass system of the kiln after it has been cleaned of alkalis and chlorides. Therefore, it contains mainly limestone but may also contain small amounts of fly ash and clinker. Both calcined clay and kiln dust may contain more chloride than PC. However, no chemical analysis was made to quantify chlorides in the raw materials.

*Table 2 – Mix design (in kg/m³) of the field exposed concrete elements. The coarse aggregates consisted of three fractions, 5/8, 8/16 and 16/25 mm. *) Grey microfiller.*

PC	CC	Filler*	*w/b*	Sand	Coarse. Agg
290.0	77.1	51.4	0.39	620.3	1086.7

For the present paper, data from an element submerged in Hirtshals harbour were used. The field exposure condition, extraction of cores, and subsequent chemical analysis are described in Ref. [14]. Even though Ref. [14] only describes handling of samples after 11 months (0.9 years), the investigation after 4.7 years of exposure was carried out in the same way. Two cores were drilled from the concrete element, one core from the submerged zone (25 cm from the bottom of the element) and one core from the splash zone (25 cm from the top of the element). For each extracted core, a chloride profile was determined by first grinding off material in layers parallel to the exposed surface of the drilled concrete cores and then performing analysis of the dust. Chloride content was determined by following a procedure similar to NT BUILD 208 [15]. However, the chloride contents were measured by potentiometric titration using a Titroline 7000 titrator rather than Volhard titration.

In addition to the concrete elements, cylinders were also cast to conduct various tests. In particular, an apparent chloride migration coefficient of $5.0 \cdot 10^{-12}$ m²/s was measured according to NT BUILD 492 [12] for the mix described in Table 2, after approx. 70 days of curing.

2.3 Modelling

Migration

For chloride migration experiments, the apparent diffusion coefficient was calculated based on the colorimetric method according to Equation (3) [12]. Note that $D_{\mathrm{m,app}}$ is also referred to as the non-steady-state chloride migration coefficient in the literature.

$$D_{\mathrm{m,app}} = \frac{0.0239(273+\theta)L}{(U-2)t} \cdot \left(x_{\mathrm{d}} - 0.0238\sqrt{\frac{(273+\theta)Lx_{\mathrm{d}}}{U-2}} \right) \tag{3}$$

where:

$D_{\mathrm{m,app}}$: Apparent diffusion coefficient from migration experiment [10^{-12} m²/s].
U: Absolute value of the applied voltage [V].
θ: Average value of the initial and final temperatures in the anolyte solution [°C].
L: Thickness of the test specimen [mm].
x_{d}: Average value of the penetration depth [mm].
t: Test duration [h].

Diffusion
For diffusion experiments, the chloride profiles were fitted using the model described by Jensen [7,8]. Jensen's model is based on a space and time discretisation of equations (2a-2c), where Jensen considered c_b in g/g gel and c_f in mol/l. Thus, to be able to make a chloride balance of the system, the mass of gel is needed. To this end, Jensen used the classical approach of Powers, which is however limited to pure PC systems. Therefore, in this study, thermodynamic modelling with GEMS [16–18] was used. The simulations were made based on the PSI-Nagra [19] and the Cemdata 18 [20] databases, and the CSHQ [21] model was used. The model used the chemical compositions of each paste constituent as inputs and returned the phase assemblage at thermodynamic equilibrium. To account for the different kinetics of hydration, the following degrees of hydrations for (PC-CC) were used in the diffusion model: PC (90, -), PCC35 (95, 60) and PCC50 (95, 30). The filler was added as pure calcium carbonate, fully available for reaction. Finally, the amount of gel was taken equal to the sum of all hydrate phases. More details on the modelling and the assumptions are presented in [9].

In a previous work [9], the Freundlich parameters, α and β, cf. Equation (2b), were determined experimentally. Subsequently, these parameters were used as inputs in Jensen's model. The model was then fitted on the experimental curves by adjusting the effective diffusion coefficient, $D_{d,eff}$, and the surface concentration, c_s, using the least squares method. The first data point at a depth of 1 mm was disregarded in the fitting.

In this work, it is proposed to use Jensen's model to determine Freundlich chloride binding parameters. To do so, the diffusion coefficient derived from migration experiments is used as an input. Moreover, the fitting algorithm was modified to handle more parameters.

2.4 Data processing

Laboratory tests
Chloride binding experiments are generally carried out for research purposes only, and the Freundlich parameters are therefore not available for input in chloride ingress models. Here, it is proposed to combine chloride migration and chloride diffusion tests to estimate the Freundlich parameters. This is done in two steps:

1) Determine the apparent diffusion coefficient from migration tests, $D_{m,app}$, according to Equation (3).
2) Fit the chloride ingress profile with Jensen's model, assuming $D_{m,app} = D_{eff}$. This assumption is based on the conclusions of [9]. The parameters to be adjusted are therefore the surface concentration and the two Freundlich parameters.

In Ref. [9], the effective diffusion coefficients from migration tests, $D_{m,eff}$, were also determined. These coefficients are more complex to obtain than $D_{m,app}$, because they require that a chloride profile of the migration test specimen is made after the migration test. Since these values were available, the analyses were also made assuming $D_{m,eff} = D_{eff}$.

Field tests
A similar procedure was applied to the field data. Chloride profiles at 0.9 and 4.7 years were fitted using Jensen's model, assuming $D_{m,app} = D_{eff}$ and adjusting the surface concentration and the Freundlich parameters. Predictions of the 4.7-year profiles were also made based on the parameters derived from the 0.9-year profiles.

It is well-known that chloride profiles usually exhibit a "peak" a few millimetres from the surface. Such a peak is likely caused by leaching [22], which is not accounted for in the present paper. Therefore, all data points between the surface and the top of the peak were disregarded. Moreover, because the initial chloride content in the concrete was not known, it was decided to use the total chloride content measured experimentally in the tail of the profiles, i.e., the furthest inwards in the concrete. The same value of 0.03 g Cl per 100 g of concrete was used throughout the analyses.

Curve fitting
Curve fitting turned out to be challenging due to the limited number of experimental data points. In particular, the least squares method, which is often used to fit Fick's law to chloride profiles, performed poorly when fitting Freundlich parameters. In this respect, a more appropriate approach was implemented, namely the Basin-hopping technique [23]. Basin-hopping is derived from the Monte-Carlo technique and is particularly efficient for solving problems with many local minima. The algorithm starts with a random guess, followed by a local minimization to find a first solution. Then, another random guess is made to "jump" out of the first local minimum, and the process is repeated. The second solution is compared to the first one and accepted if (1) it is better or (2) it helps to escape a local minimum.

In this work, a twofold stopping criterion was applied: (1) 500 iterations maximum or (2) five iterations in a row without any improvement. Local minimization was made with the L-BFGS-B algorithm, a quasi-Newton method where the parameters are constrained.

3. RESULTS AND DISCUSSION

3.1 Processing of diffusion curves

Figures 3 and 4 show the experimental ingress curves obtained in the chloride diffusion experiments, together with the bound and free chlorides as determined by Jensen's model. In Figure 3, it was assumed that $D_{eff} = D_{m,app}$; in Figure 4, it was assumed that $D_{eff} = D_{m,eff}$. The same D_m, determined after 12 weeks of curing, were used to fit the 12 and 30-week profiles. However, Figure 1 shows that such approach likely overestimates the average effective diffusion coefficient, which is somewhere in between D_m determined after 4 w and 12 w of curing.

These Freundlich parameters determined with an "indirect" method are presented in Table 3, together with the ones from "direct" binding isotherms. A graphical representation of the corresponding Freundlich isotherms is presented in Figure 5, together with the experimental data points.

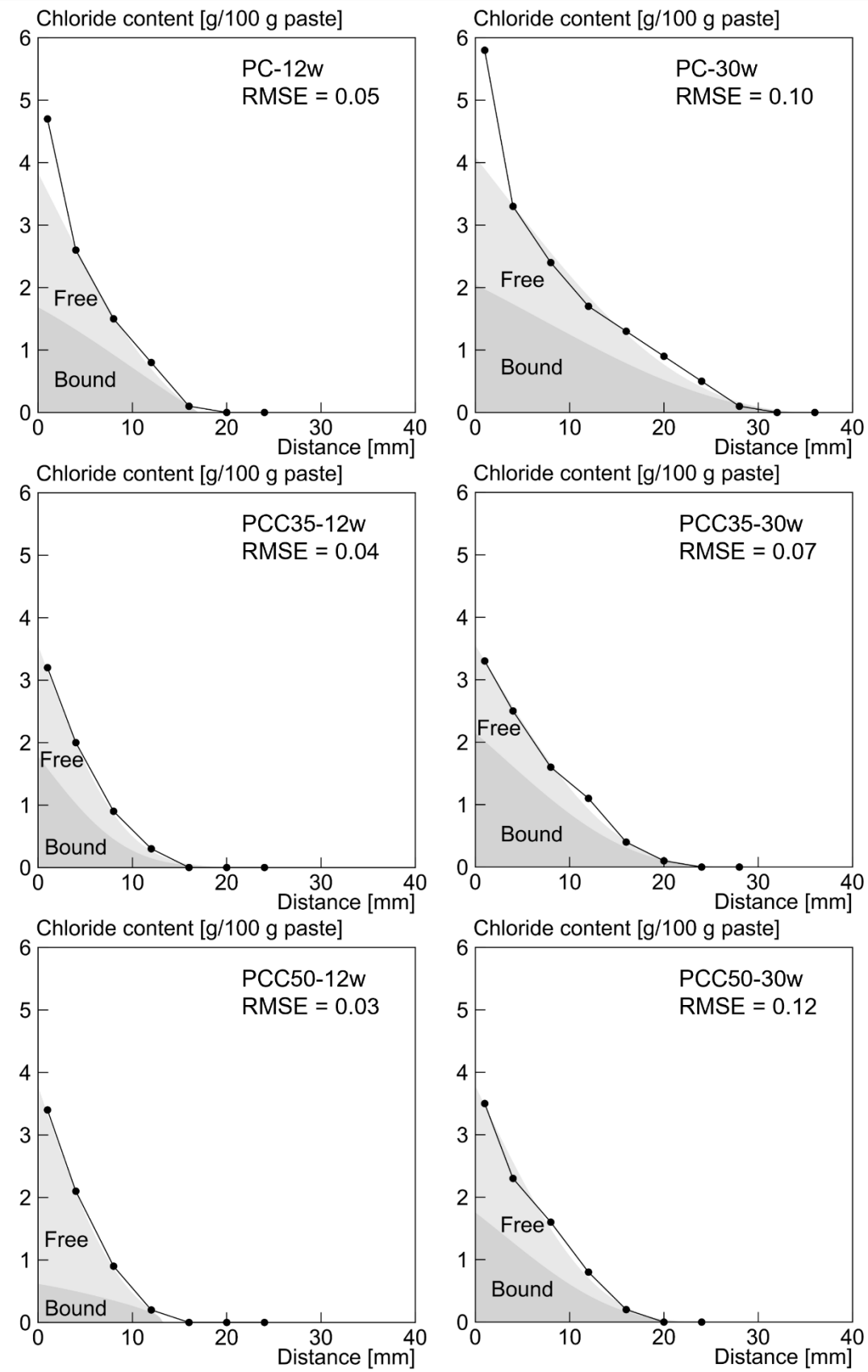

Figure 3 – Bound, and free chloride profiles obtained with Jensen's model (shaded areas) assuming $D_{eff} = D_{m,app}$, and experimental total chloride profiles (black solid line). For PC, the point closest to the surface was disregarded in the fitting. RMSE = root mean square error.

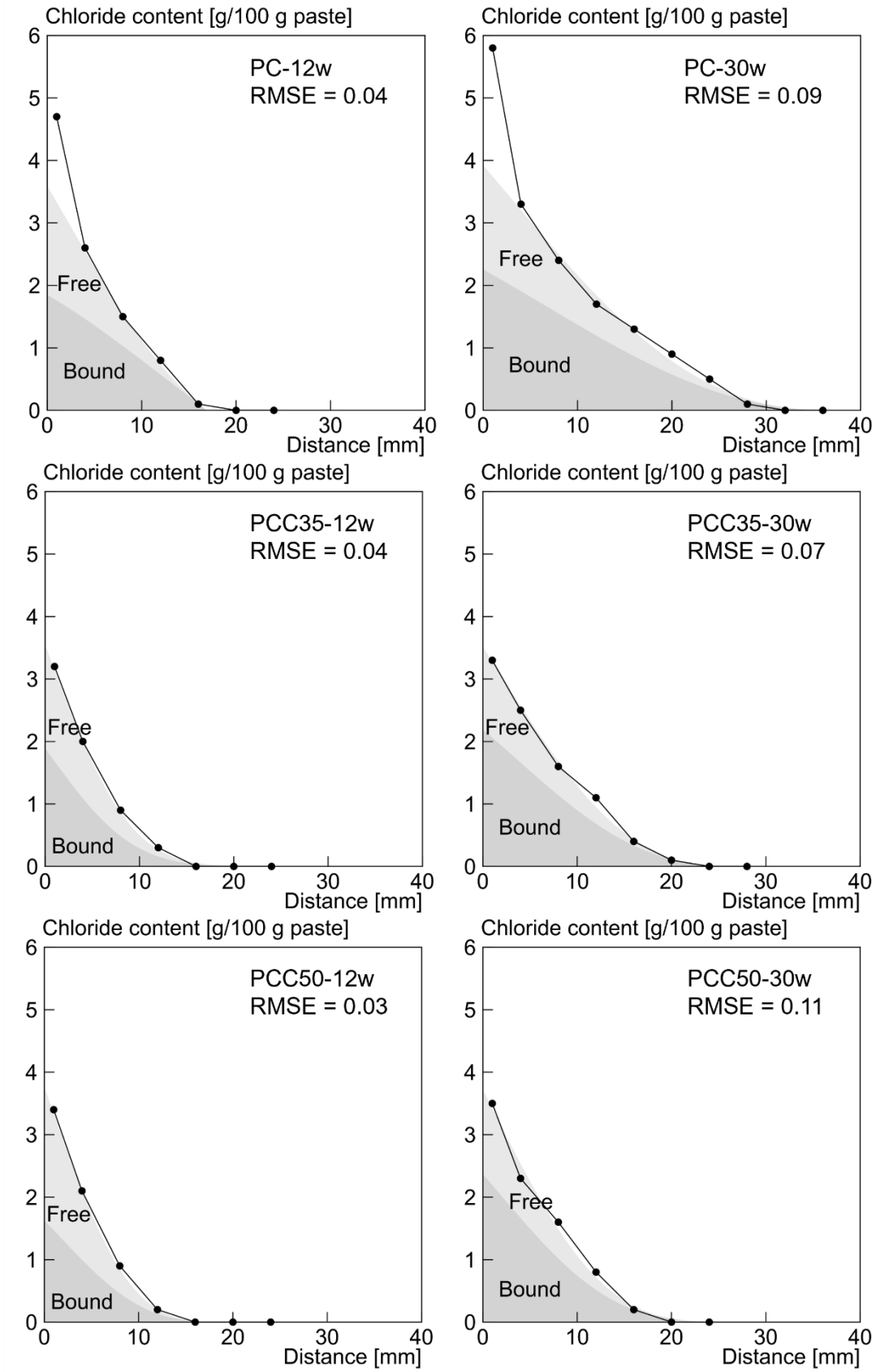

Figure 4 – Bound, and free chloride profiles obtained with Jensen's model (shaded areas) assuming $D_{eff} = D_{m,eff}$, and experimental total chloride profiles (black solid line). For PC, the point closest to the surface was disregarded in the fitting. RMSE = root mean square error.

Table 3 – Freundlich parameters, α and β, determined experimentally (direct) and by curve fitting (indirect) of chloride profiles after 12 and 30 weeks. Indirect determinations were made using apparent and effective diffusion coefficients derived from migration experiments after 12 weeks of curing.

Binder	Direct Binding isotherm		Indirect – Curve fitting					
			Type	D_m [10^{-12} m^2/s]	12 weeks		30 weeks	
	α	β			α	β	α	β
PC	6.5	0.87	Apparent	13.0	7.3	0.49	6.8	0.65
			Effective	16.0	8.9	0.40	8.3	0.67
PCC35	12.3	0.45	Apparent	8.3	8.1	0.92	14.1	0.75
			Effective	8.9	9.1	0.92	15.3	0.73
PCC50	12.3	0.40	Apparent	4.8	5.8	0.44	11.9	0.71
			Effective	7.3	10.2	0.74	18.8	0.80

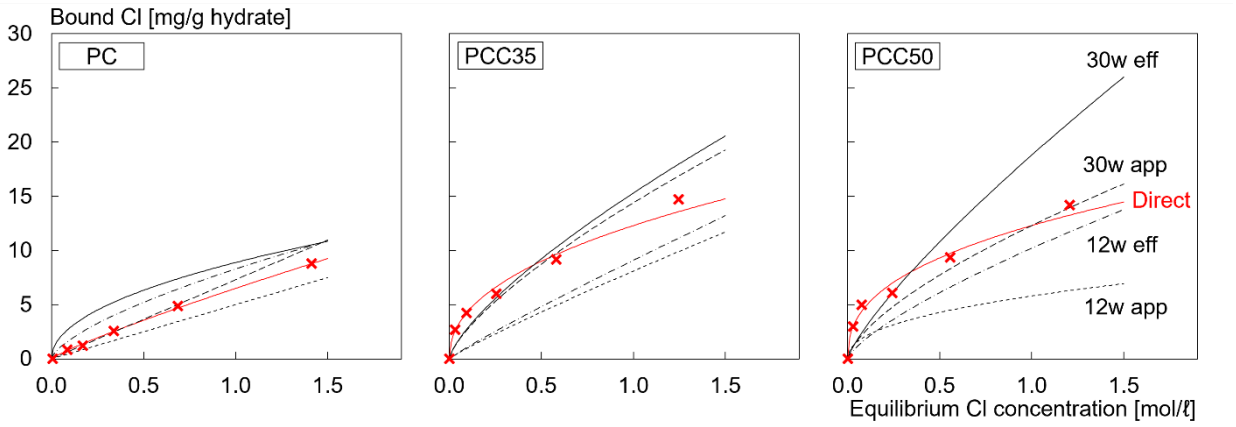

Figure 5 – Chloride binding isotherms drawn with the Freundlich parameters from Table 3. The red crosses represent experimental data on which the "Direct" curves were fitted.

Figures 3 and 4 show that the modelled profiles are in agreement with the experimental data for all binders and exposure times. Overall, the Freundlich parameters derived from curve fitting of the 30-week data lead to binding isotherms that are fairly close to those measured in dedicated experiments for PC and PCC35, represented by the red crosses in Figure 5. For PCC50, the results significantly differ whether $D_{m,app}$ or $D_{m,eff}$ is used. This is due to the fact that PCC50 has the smallest values for D_m for the largest absolute differences between apparent and effective, and between 12 w and 30 weeks. Such phenomenon may be linked to the degree of reaction of the calcined clay. For a given binder, a fixed degree of reaction was assumed, independent of the curing time. However, the degree of reaction would likely increase between 12 and 30 weeks, implying more hydrates and thus more chlorides being bound. Consequently, the microstructure of the paste would also be refined, which could explain the significant drop of the diffusion coefficient.

The Freundlich parameters determined from the 12-week data result in binding isotherms that tend to be below the other curves, which means less binding. This could be expected because these

samples had less maturity, which was not accounted for when estimating the amount of hydrate by thermodynamic modelling. It should be noted that the Freundlich equation does not exactly match the trend given by the experimental points for PCC. The Freundlich equation results in a curve with a soft bend, whereas the experimental data suggest a sharp bend at an equilibrium Cl concentration of approx. 0.1 mol/ℓ, and at higher equilibrium concentrations, the relation between free and bound chlorides seems to be almost linear. The Freundlich isotherm is an empirical relationship; possibly other empirical relationships may fit data better, but it is outside the scope of the present paper to investigate other chloride binding models. However, the approach presented here is not specific to Freundlich isotherms, so it may be adapted to other chloride binding models.

As mentioned in the legend of Figures 3 and 4, for PC, the points closest to the surface were disregarded as they did not seem to fit with the overall shape of the profile. For comparison, Figure 6 presents the profiles obtained by including these points in the fitting. Such additions result in a lower fitting quality, as shown by the larger RMSE. Moreover, the β parameters above 1 imply that the corresponding binding isotherms are convex, which does not correspond to the concave shape observed experimentally.

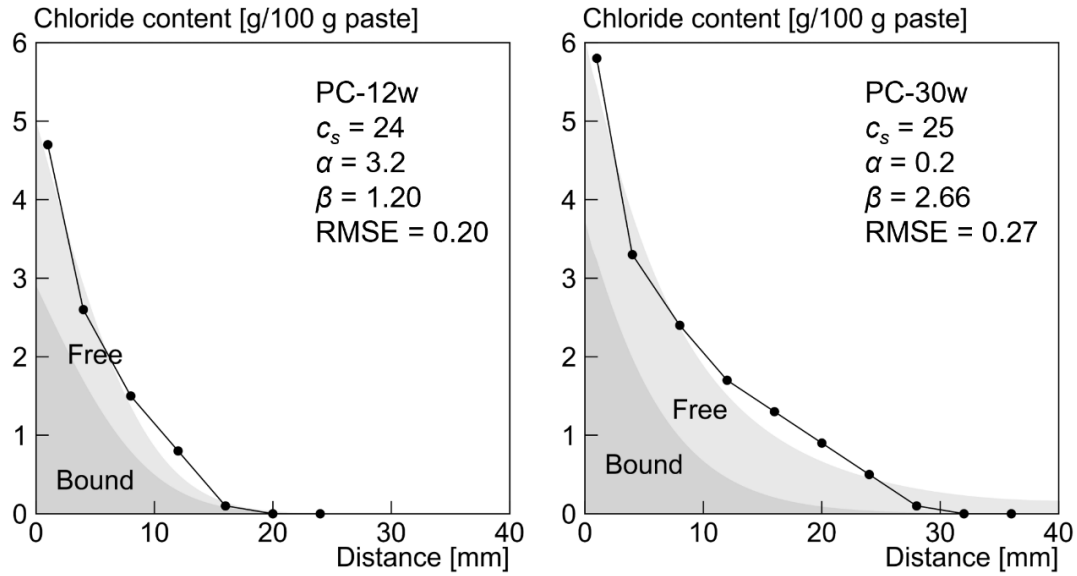

Figure 6 – Bound and free chloride profiles obtained with Jensen's model (shaded areas) assuming $D_{eff} = D_{m,app}$, and experimental total chloride profiles (black solid lines). Contrary to Figure 3, the point closest to the surface was included in the fitting. RMSE = root mean square error.

Based on these observations, it is suggested to disregard the points closest to the surface in the fitting, if these points do not reasonably match the overall trend. Such behaviour is only observed with PC, and the cause is unexplained.

3.2 Case study with field data

The same methodology was applied to field data. It should be underlined that the field samples were not made with the exact same binders and *w/b*, so they cannot be used as a proper test of the model. However, the following intends to verify whether the proposed method leads to the expected order of size for the results.

Figure 7 presents the results from the model, together with the experimental data for two different ages, 0.9 and 4.7 years, and two exposure locations, submerged and splash zone. The outputs from the fitting are presented in Table 4. As mentioned previously, the diffusion coefficient was kept constant at $5.0 \cdot 10^{-12}$ m^2/s, corresponding to the apparent diffusion coefficient measured on concrete cylinders cast from the same batch with chloride migration, $D_{m,app}$.

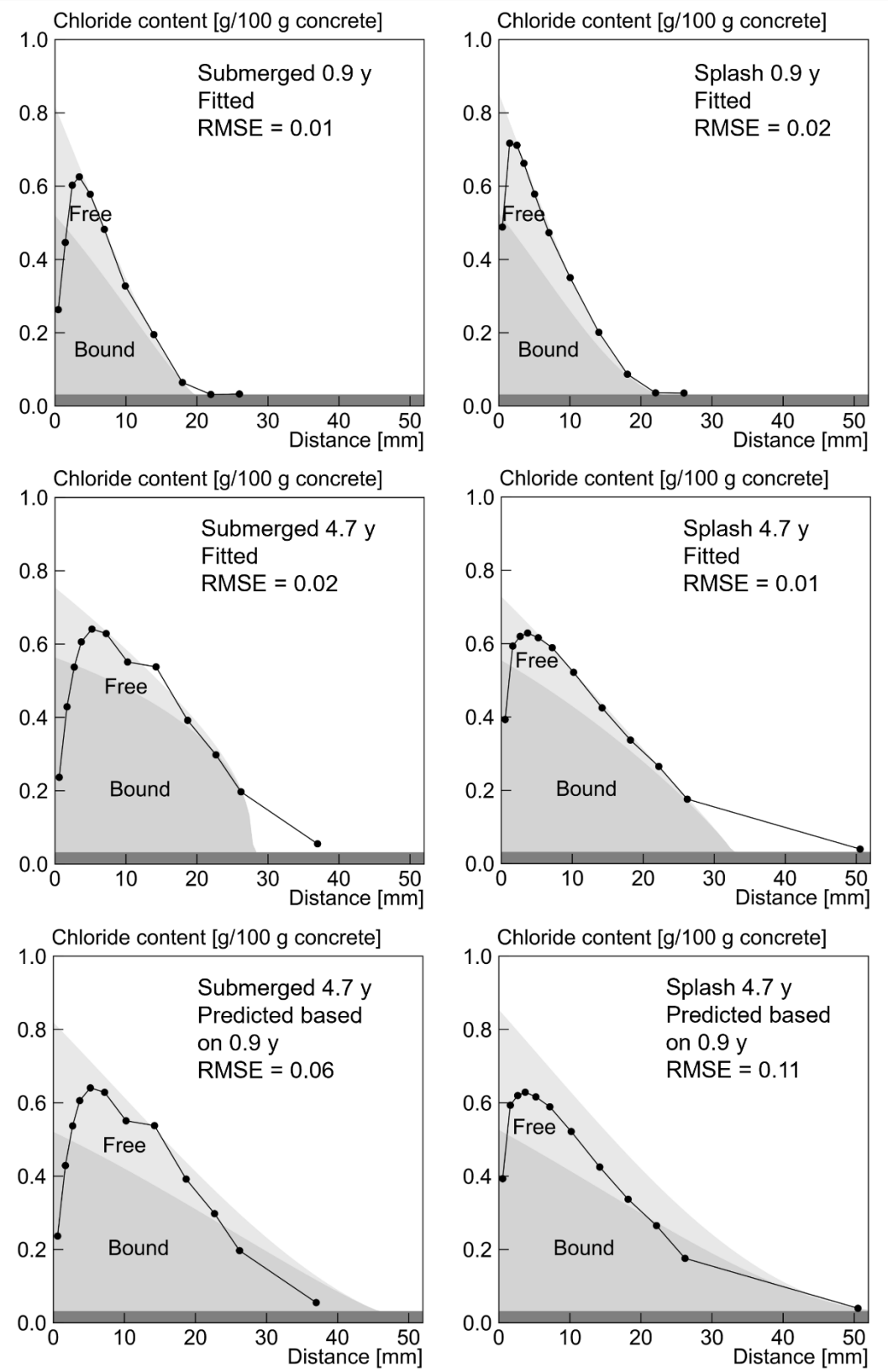

Figure 7 – Comparison between Jensen's model (shaded areas) and experimental total chloride profiles (black solid lines) from the field exposure site at Hirshals. The dark grey horizontal stripe corresponds to the initial chloride content. The diffusion coefficient was kept constant at $5.0 \cdot 10^{-12}$ *m²/s. In the lower row, the 4.7 year-profiles were predicted using the outputs of the fitting at 0.9 years. RMSE = root mean square error.*

Table 4 – Fitted parameters obtained with Jensen's model on field data.

Parameter	Submerged zone		Splash zone	
	0.9 years	4.7 years	0.9 years	4.7 years
D_{eff} [10^{-12} m/s^2]	5.0	5.0	5.0	5.0
c_s [g/100 g paste]	13.7	8.8	15.1	8.0
α	12.0	20.5	10.1	17.9
β	0.53	0.29	0.62	0.47

The modelled profiles at 0.9 years are in agreement with the experimental data, for both locations. However, using the parameters determined at 0.9 years to predict the 4.7-year profiles results in overestimating chloride ingress. Fitting the 4.7-year profiles leads to larger α and smaller β values, which implies more binding and, therefore, less ingress. It should be mentioned that the same diffusion coefficient was used. Therefore, the potential refinement and depercolation of the microstructure between 0.9 and 4.7 years was not accounted for and may cause the overestimation. The shape of the binding isotherms based on the Freundlich parameters from Table 4 is shown in Figure 8. Since the binder used for the field specimens differs from PCC35, it is difficult to evaluate the accuracy of the α and β parameters shown in Table 4. However, comparing the 0.9-year data in the field with the 30-week (0.6-year) data in the laboratory for PCC35 shows that both α and β have comparable orders of size.

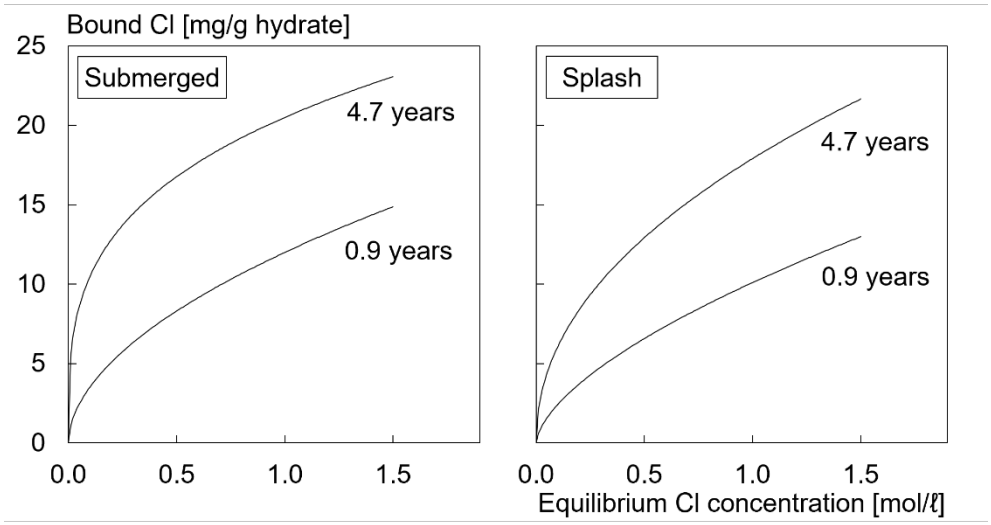

Figure 8: Chloride binding isotherms based on the parameters from Table 4.

Even though the RMSE is relatively low for the 4.7-year fitted data, the modelled profile for the submerged location shows a sharp concave drop around 27 mm, which differs from the more linear or slightly convex profiles in the other cases. Such behaviour might be a consequence of fewer data points included in the fitting – 7 points versus 8 or 9 for the others.

4. APPLICABILITY AND RESEARCH NEEDS

4.1 Applicability

The approach presented in this paper allows the determination of Freundlich chloride binding parameters, without performing dedicated chloride binding experiments. The approach is based on the results of two standard test procedures, which are routinely conducted in material testing laboratories: Chloride migration and chloride diffusion. By combining the outcomes of both tests, one can not only determine the diffusion coefficient, but also chloride binding parameters, which affect chloride ingress and therefore its prediction [6]. In other words, one extra information can be derived from already used tests, without additional laboratory work. Thus, it will avoid chloride binding isotherm experiments, which require time to equilibrate – 6 weeks is this study – and special measures against leaching which requires extra material as explained in Section 2.2.

This work could also be used when documenting new binders. As an example, the Danish standard DS 206 requires conducting NT BUILD 492 (chloride migration) on samples cured for up to 180 days to document new binders. The derived diffusion coefficients are then compared to those of "well-known" binders, to qualify the new binder for a certain exposure class. In this respect, one could consider including chloride binding parameters in the comparison, to make a more realistic comparison between binders.

The modelling contains two parts: (1) a space and time discretisation of the governing equations of chloride ingress, and (2) thermodynamic modelling, e.g., with GEMS. While (1) is relatively straightforward, (2) requires the use of a dedicated software, which may limit its use to experienced users. However, thermodynamic modelling gives the possibility to virtually model any system, so that the binder composition and the *w/b* can be accounted for. It should be emphasised that the thermodynamic model itself should be validated before being used in a chloride ingress model.

4.2 Research needs

This paper is a first attempt to determine chloride binding parameters without performing separate experiments on this. However, more investigations could strengthen the approach and its applicability.

Even though different binders were studied, extending the experimental matrix to more binders would allow a better quantitative assessment of the accuracy of the method. Such matrix could include traditional supplementary cementitious materials (SCMs) like fly ash, silica fume and blast furnace slag, which have been used in concrete structures exposed to chlorides. In this way, it may be possible to have long-term field data to validate the approach. Emerging SCMs could also be included, to assess the applicability of the method to less-known systems – in particular with respect to thermodynamic modelling. Finally, the *w/b* may also be relevant as a variable in a parametric study.

Another parameter of interest would be the curing time before conducting chloride migration and diffusion tests. It was observed that the diffusion coefficient for PCC50 dropped significantly – around 50%, between 12 and 30 weeks [9]. PCC50 also shows the largest scatter among the different curves in Figure 5, which may be linked to ongoing hydration between the two durations. Ideally, the tests should be conducted on samples in which the constituents have reached a degree of reaction close to their maximum potential.

The work presented here assumes chloride binding to follow a Freundlich isotherm. However, other models may better represent chloride binding [3,24], which could be tested. The model would have to be adapted by changing the governing equation of chloride binding, Equation (2b), but the approach remains valid. Such investigations do not require more experimental work, so that multiple models could be tested on the systems mentioned in the previous paragraph.

Finally, testing more systems and processing the results with different chloride binding models would constitute a database that could then be analysed with respect to current regulations on binders for example. It could be investigated if having the extra knowledge of chloride binding parameters would lead to different choices when qualifying a binder for a certain use.

5. CONCLUSIONS

Chloride ingress was modelled with a mechanistic model considering Fick's second law and a Freundlich relationship between free and bound chlorides. The focus was on estimating the Freundlich parameters from chloride profiles, without actually performing dedicated chloride binding experiments. This study intended to introduce a suitable approach, and present examples of application. The following conclusions can be drawn:

- Three cementitious systems were tested: Pure Portland cement, and ternary blends with 35 and 50% clinker replacement with calcined clay and limestone. For these systems, it was possible to estimate Freundlich parameters by fitting chloride diffusion profiles, provided that the effective diffusion coefficient is used as an input. The effective diffusion coefficient can, e.g., be derived from a relatively simple migration experiment.
- Such an approach relies on two standard tests that are routinely conducted: Chloride migration and chloride diffusion. Therefore, no extra laboratory work is required compared to what is done today.
- The approach seems applicable to natural chloride exposure, but a more comprehensive study is needed to determine a clear protocol.
- The quality and the number of experimental data points are important for the fitting.

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