Modelling of chloride ingress in concrete based on benchmarking field results

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Abstract. Modelling the ingress of chloride ions into the cover of a concrete structure is a phenomenon that is gaining an increasing attention of the research community, but even more, from the engineering practice. As the mechanism that drives the ingress of chlorides is implicitly responsible for the service-life of concrete structures, its input parameters are a major issue whenever predicting the service-life of new concrete structures. In this paper most relevant parameters involved in the evaluation of chloride ingress models are discussed and related to the benchmark activities that currently run in RILEM TC 270-CIM on benchmarking Chloride Ingress Models. The results provide an overview of the models used in the structural design stage, mostly analytical models, and in the rehabilitation stage, mostly numerical models.

1 Introduction

Current models used to predict the (remaining) service of reinforced concrete structures are mostly based on the ingress of chlorides with time. As these chlorides enter the concrete cover, they will slowly move towards the reinforcement bars and harm the passive layer that protects the bars from corroding. Until reaching this stage, the ingress is in a so called “initiation stage”, while after this stage, a more detrimental process will appear which is called the “propagation stage”. Actually, these terms are based on the Tuutti model who proposed this schematisation already in 1982 [1]. For modellers this categorisation of chloride ingress into the concrete cover also very convenient as it separates the mechanism that drives steel corrosion in concrete into a physical-chemical transport part (initiation) and a damage and fracture mechanical part (propagation).

Fig. 1: Schematic sketch of steel corrosion sequence in concrete [1].

In general terms, the first period in which the chlorides enter the concrete cover zone via the pore structure is the most important one in terms of prevention of damage and implicit for the elongation of service-life of concrete structures. In order to achieve this, the pore size, pore morphology and pore connectivity at the surface should be controlled by the quality of the paste and the implicit thickness of the surface paste layer, driven by the large aggregate sizes (*wall-effect*). With these, the boundary conditions of the adjoining open pore area is the parameter that provides chlorides the opportunity to enter the concrete surface. From this point on, the amount of chlorides at the concrete surface, determine the concentration at which the chloride transport mechanism will be exposed to. Modellers call this is the boundary condition, which is driving the chloride ingress mechanism and is depending on the exposition class of a concrete structure. It is mostly expressed in terms of the chloride concentration relative to the amount of cement applied in a concrete. However, sometimes also the concrete density is used as reference for the chloride concentration. Once chlorides enter the concrete a force is needed that causes them to move through the pore system into the direction of the reinforcement. Generally, this is the so-called concentration gradient, which is a force that is depending on the concentration differences between the chlorides over a certain distance. In the concrete cover it is clear that the chloride concentration at the surface is highest (boundary condition) and towards the inside of the material, it approaching the initial chloride concentration of the concrete mixture. This lower level concentration is representing by the amount of chlorides allowed to be present in a concrete according to the codes and

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standards. The chloride concentration gradient over the cover thickness is the major player in a chloride ingress model, since it is one of the reasons that chlorides actually start to move. If this gradient would not exist, chlorides would stay where they are and the service life would be much longer and determined by another damage mechanism that causes the concrete to deteriorate. Another reason that affects the rate at which chlorides move through the pore structure of a cover is the diffusion coefficient, which is the rate determining parameter that linearly affects the movement of the chlorides through the concrete cover. How these parameters are taken into account in chloride ingress models, what their main impacts are, and how they finally affect the simulation result will be presented in this paper. The paper also reflects the issues that are point of discussion of the RILEM TC 270-CIM which is on “Benchmarking Chloride Ingress Models on Real-life Case Studies: Theory and Practice”, and is currently active with the aim to develop a STAR and recommendation on chloride ingress modelling.

2 APPARENT DIFFUSION

2.1. Diffusion mechanism

Diffusion is a phenomenon where species move through a medium while driven by concentration differences. According to an official (chemistry) definition it is “the process whereby particles of liquids, gases, or solids interact as the result of their spontaneous movement caused by thermal agitation and in dissolved substances move from a region of higher to one of lower concentration [2]”. From this definition, it becomes clear that, (from a modellers point of view), this mechanism needs a medium, diffusing species and a driving force. Mapping this situation to the situation that prevails in a concrete cover results in the following associating components, which are, pore water (medium), chloride ions (species), and chloride concentration difference (driving force). It makes implicitly clear that the pore water is the medium that facilitates the movement of chlorides. This also means that without pore water (dry pores) there can be no chloride diffusion. This makes those pores, which are partly saturated even more interesting since also the pore humidity comes into play, making the chloride ingress mechanism much more complex. It leads to a situation, where also surface carbonation may affect chloride movement to a large extent. Regarding the occurrence of chloride ions in a porous system, simply speaking, in cement-based materials there are two situations in-which they may appear. This is the situation that chloride ions may move freely in the medium or they can be chemically or physically bounded to the inner pore wall areas existing of hydration products like Friedel’s salt or C-S-H [3] (see Fig 2). From a modellers perspective, the chlorides may exist in two different ways. These are 1) bound chlorides, in this case they are fixed to the pore wall areas and depending on the local conditions like concentration and/or pH possibly turn into free chlorides

Fig 2 : Schematic representation of free and bounded chloride ions in a liquid medium like pore water [3].

again, and 2) free chlorides, which are those that are able to move through the pore medium driven by concentration gradients. Bound chlorides are either the result of chemical binding, i.e. chloride ions are chemically bound by reacting with the cement hydrates or physical binding, i.e. chloride ions are physically adsorbed to the cement gel. The total chloride content in cement-based material is a sum of free and bound chlorides. It is important to know that only free chlorides are able to move (diffuse) through a pore solution in a pore structure of a cement-based material. From this it becomes clear that only the free chlorides in a system “travel” and may reach the surface of steel rebars and inducing depassivation and associated corrosion of the steel rebars. Therefore, it has to be noticed that steel corrosion is only related to the free chlorides that are active in the pore solution. It is, therefore, possible to simulate chloride diffusion in a cement-based material only in terms of total chloride concentrations. This strategy is mostly adopted in analytical models like the DuraCrete model [4] based on modified Fick’s 2nd law, where chlorides binding effects are very difficult to include. Schematizing this situation of free and bound chlorides leads to the situation that the total chloride concentration C_t is the summation of free chloride concentration C_f and bound chloride concentration C_b as $C_t = C_f + C_b$. Whenever considering these two components in the second order differential equation for diffusion processes (called Fick’s second law), the following situation appears [5][6]:

$$\frac{\partial C_t}{\partial t} = \frac{\partial C_f}{\partial t} + \frac{\partial C_b}{\partial t} = \left(1 + \frac{\partial C_b}{\partial C_f}\right) \frac{\partial C_f}{\partial t} \quad (1)$$

$$\frac{\partial C_f}{\partial t} = \frac{D_e}{\left(1 + \frac{\partial C_b}{\partial C_f}\right)} \frac{\partial^2 C_f}{\partial x^2} = D_a \frac{\partial^2 C_f}{\partial x^2} \quad (2)$$

where D_a represents the apparent chloride diffusion coefficient that is a function of the effective chloride diffusion coefficient D_e and chloride binding capacity $\partial C_b / \partial C_f$. The factor $\partial C_b / \partial C_f$ represents the influence of chloride binding on the chloride diffusion coefficient and varies largely with the free chloride concentration C_f and the local chemical and physical conditions surface energy and/or pH. Therefore, the apparent chloride

diffusion coefficient D_a is not a constant but relates to the effective chloride diffusion coefficient D_e and the free chloride concentration C_f , both of which depend upon the microstructure of cement-based materials.

2.2 Free chlorides

As addressed before, free chlorides are those that are free to move through a pore structure and relate to the apparent diffusion coefficient D_a , which implicitly means that chloride binding, and other microstructural changes are not considered. From a modellers point of view, the differential equation that drives this process is the well-known Fick's second law which can be formulated as:

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \quad (3)$$

where, D_a is the diffusion coefficient, C is the chloride concentration of those ions that can freely move through the pore system. In Fig. 3, this principle is schematically shown, while distinguishing between the free and bounded chlorides. This approach leads to the possibility to derive a closed analytical solution, which is also known from the DuraCrete approach. In this case it results in the well known equation [7][8]:

$$C(x, t) = C_s - (C_s - C_i) \cdot \operatorname{erf}\left(\frac{x}{2 \cdot \sqrt{D_{app}(t) \cdot t}}\right) \quad (4)$$

where $C(x, t)$ is the local concentration of chlorides that diffuse into the concrete cover zone, C_s the surface chloride concentration (constant), and C_i the initial chloride concentration in the concrete. The parameter x is the distance inside the cover, t the time and $D_{app}(t)$ the so-called apparent diffusion coefficient, not considering the bound chlorides. When applying this formula in the way it is written in (4), with a time dependent $D_{app}(t)$, it is important to know that all other boundary conditions are considered to be constant in time and space. The time dependence of the diffusion coefficient is based on a simple formulation introduced also in the DuraCrete model and is denoted as [7][8]:

$$D_{app}(t) = D_{app}(t_0) \cdot \left(\frac{t_0}{t}\right)^m \quad (5)$$

This well-known formula for the apparent diffusion of concrete represents the apparent diffusion at 28 days of hardening $D_{app}(t_0)$, multiplied with a time factor (t_0/t) to the power m , which is called ageing factor. With this ageing factor the influence of several uncertainties of the behaviour of the concrete pore structure with time are taken into account. It is generally assumed that ageing will lead to a reduction of the pore space, or with this, to a reduction of the diffusivity of the cementitious material. According the fib-Model Code 2010 [8], this is

Fig. 3 : Schematic representation of free and bound chlorides in a saturated pore.

due to the following reasons :

- the continued reaction of the binder, in particular when pozzolans and slag are used ;
- the influence of capillary suction of water in the surface zone (decreasing with time);
- the degree of saturation of concrete ;
- in this respect, the beneficial effect of penetrated chlorides from the seawater of de-icing salt leading to ion exchange with subsequent pore-blocking in the surface layer.

In the scientific, but also in the current practice, there is a lot of discussion going on about the impact the ageing factor has on the prediction of the service life of concrete structures. As the factor is missing a real physical background it can be considered as a kind of fit factor that should be calibrated on any structure in particular. This means that for existing structures, this factor works reasonably well as it can be calibrated on the data received from chloride induced concrete structures. For new structures, this factor is under strong discussions as cannot be calibrated [9] and predictions may be unreliable. In that particular case its value should be “assumed”, or based on expert judgements. This often leads to extreme uncertainties in the probabilistic service-life assessment simulations. This is one of the reasons that the RILEM TC 270-CIM committee wants to try to figure out whether a more fundamental background for the ageing effect on the diffusivity can be detected, using benchmarking on field results. For this, the committee is comparing various analytical and numerical model results done on chloride ingress data at various ages. It should enable a first view on the main factor that influence this so-called ageing factor. As the committee is still under way, results will be published in Materials & Structures and a RILEM STAR report.

2.3 Chloride binding

The binding of chlorides in a chemical or physical way (see also Fig 2) is a phenomenon that can also be considered explicitly in analytical design models for the prediction of chloride ingress [4,5] and/or associated service-life predictions. Numerical models [10] have already advanced numerical approaches implemented to account for this phenomenon explicitly. However, for

design models, often an engineering approach is requested forcing modellers to come up with improved analytical solutions. When considering the process of chloride binding more explicitly, ions penetrate into cement-based materials where some of them can be captured and immobilized by the hydration products [6]. This process of interaction between the chloride ions and cement hydrates is known as chloride binding. Although the mechanisms of chloride binding is still quite unclear, it is a common view that two types are involved in chloride binding: one is the physical binding by calcium silicate hydrate (C-S-H) gel, and the other is the chemical binding by some of the hydration products. Chloride binding may narrow the pore structure of cement-based materials, leading to a decrease in chloride diffusivity [6]. In order to include the binding of chlorides in the description of the model, it is essential to establish the quantitative relationship between the bound chloride concentration C_b and free chloride concentration C_f over a range of chloride concentrations at a given temperature, which is referred to as the chloride binding isotherm. In the literature (see e.g. [10,11]), four types of chloride binding isotherms, i.e. linear, Langmuir, Freundlich and BET binding isotherms, can be found where the Langmuir isotherm is quite often used to simulate the effect of binding in chloride ingress modelling [10]. The differential equation that includes the binding effect and, with this, separates the chlorides in a free and bound part can be denoted as (see also Fig. 4 and Fig 5):

$$P \frac{\partial C_f}{\partial t} = -D_e \frac{\partial^2 C_f}{\partial x^2} - (1-P) \rho_s \frac{\partial C_b}{\partial t} \quad (6)$$

where C_f is the total chloride concentration, C_b the bound chloride concentration, D_e the effective diffusion coefficient, ρ_s the density of solids in concrete and P the concrete porosity. With this equation, the relation between the bound and free can be denoted as [11]:

$$C_t = P C_f + (1-P) \rho_s C_b \quad (7)$$

which makes clear that the total amount of chlorides is the summation of both these two chloride containing components. The approach was also discussed during the RILEM TC 270-CIM benchmarks as a possible solution to separate between bound and free chlorides. If a chemical reaction rate for chloride binding is faster than diffusion, an equilibrium between free and bound chlorides is assured. This allows modelers to employ binding isotherm, for example using Langmuir:

$$C_b = \frac{K_{eq} C_{max} c}{1 + K_{eq} c} \quad (8)$$

Then the reaction rate term for chloride ions binding is:

$$r = (1-p) \rho_s \frac{\partial C_b}{\partial t} = (1-p) \rho_s \frac{\partial C_b}{\partial c} \frac{\partial c}{\partial t} \quad (9)$$

where the required differential term is obtained by differentiating the Langmuir binding isotherm Eq (8),

Fig. 4 : Relationship between free and bound chlorides based on the Langmuir binding isotherm.

Fig 5: Example of simulation which differentiates between free and bound chlorides based on Langmuir.

with respect to free chloride concentration c :

$$\frac{\partial C_b}{\partial c} = \frac{K_{eq} C_{max}}{K_{eq} c + 1} - \frac{K_{eq}^2 C_{max} c}{(K_{eq} c + 1)^2} \quad (10)$$

2.4 Boundary conditions

In order to solve the partial differential equation (6) boundary and starting conditions in time and space domain are required. For a chloride ingress simulation these conditions are related to the initial chloride concentration in the concrete and the surface chloride concentration. For analytical solutions like eq. (4), both the boundary as well as the starting condition are constant in time and space. This means that this condition is implicit part of the predictability performance of these classes of models. For numerical solutions, these conditions may change during in time domain. Numerical models use numerical mathematics to solve the differential equation in an explicit or implicit way. These models have lots of flexibility and are more suitable to schematize complex chloride ingress problems, also when something changes during service-life at the concrete boundary. Meaning, the boundary

Fig. 6 : Carbonation front of sample with tile taken from 40-year old tunnel wall [12].

conditions are not constant but follow a certain pattern. This could be, either a measure that hampers chlorides to enter the concrete cover (surface was covered with tiles after some time), or that a surface coating was applied, acting as a hydrophobic protection layer. This latter measure has been applied several times in precast tunnels where tiles were applied after a couple of years to avoid dissolved de-icing salts to spray against the concrete tunnel walls [12] (Fig. 6), allowing high concentrations of dissolved chlorides to penetrate into the concrete cover. In a way, these kinds of time dependent chloride concentration effects at the boundary are happening mostly at existing structures, and can therefore, only be simulated properly whenever using numerical models. The importance of applying boundary conditions in a correct way can also be considered from a different perspective like for instance the sample size. Whenever applying the analytical solution for chloride ingress simulations, a semi-infinite model is considered. In many cases this is an acceptable assumption since the cover thickness (focus area) is much smaller than the wall thickness of the concrete under consideration. In Fig. 7, it can be observed that the semi-infinite space should here at least 180 mm in order to simulate the 100 year function for the chloride profile. However, when the sample size is much smaller, like for instance is very of the case in lab or research conditions, the situation is often far from a semi-infinite situation. For example when testing long-term chloride ingress profiles using cubes of 100x100 mm². In this case, given a size range of the cover thickness of 40 – 60 mm, the situation is not a semi-infinite anymore, but rather a finite space where chloride concentrations may affect each other. In Fig. 8, the impact of the sample size and surface chloride concentrations driving chloride movements from two sides, or in case of a cube even from three sides, may be significant. Especially in the centre of the specimen, a higher chloride concentration is to be expected due to the superposition of chlorides. The figure shows a 2D approach of 3D samples, which shows that even this 2D model underestimates the chloride concentration in the center of the specimen, addressing

Fig. 7 : Example of an semi-infinite space applied for chloride ingress simulations.

Fig. 8 : Example of a finite space (cube 100 x 100 mm²) submerged in seawater at different ages.

the impact of boundary conditions for small-sample situations. Regarding the boundary conditions, two additional conditions that may seriously influence the behaviour of chlorides in a concrete cover are the environmental parameters temperature and relative humidity. The way in which the chemical activity of the chloride ions moving in a pore liquid may be effected by either a temperature enhancement or a relative humidity change can be taken into account by multiplying the diffusion coefficient by a temperature and/or relative humidity factor [13]. For engineering purposes, the temperature effect can be sufficiently accurate described with the Arrhenius function, and for the relative humidity a common function can be applied [13].

3 Benchmarking chloride ingress

The actually running RILEM TC 270-CIM has a time-frame of 2016 – 2020 [14]. Main objective this TC, which can also be read from the RILEM website [14], is to benchmark the currently available models on the

ingress of chlorides into the concrete cover using real-life case studies. The models can be either engineering- or scientifically-based and may cover the assessment, design or engineering stage of concretes exposed to different climatic conditions, such as marine, road or near shore. The benchmark will be based on a limited variety of real-life case studies that are representative for concrete structures exposed to chloride-laden environments, and where the experimental data has been received from destructive or non-destructive testing methods. Major goal of this benchmark is to allow for a critical evaluation of the performance and applicability of chloride ingress models on their practical usability, and to identify possible gaps in accuracy, coverage and/or knowledge cross-links. The scope will be limited to reinforced concretes in cracked and/or un-cracked conditions. The proposed benchmark may serve as a reference tool for current and future generations of chloride ingress models, and it can provide academics, engineers and/or asset owners an instrument to evaluate the performance of such models used for service-life assessment. The results will be reported in a RILEM STAR report. In total 14 models from different research groups all around the globe are participating in the benchmark. As the committee is now running for two years the first preliminary results are available and shows very nice and promising views. Main differences in chloride ingress simulations are caused by differences in applied boundary conditions, ageing factor, but also type of model used (numerical or analytical), and whether a model is capable of taking chloride binding explicitly into account. Due to the wide spread in modelling approaches and type of models that participated in the benchmark, it was decided to do an additional benchmark cycle with the objective to back-calculate the results and analyse whether a deeper understanding of the effect of the ageing factor on the chloride ingress results can be found. In addition to this, models are calibrated on data from measured from three typical situations, which are a marine condition, a parking lot situation and a tunnel wall. As said, after finishing the benchmark simulations, the committee will report their work in Materials & Structures and in a RILEM State of the Art Report.

4 Conclusion

Current paper gives an impression about most relevant aspects that play a role when benchmarking chloride ingress models. The parameters addressed are all relevant when evaluating chloride ingress models like is currently done in the RILEM 270-CIM on Benchmarking Chloride Ingress Models. For this a large international group of modellers are working together to set the direction for the next generation of chloride ingress models and to try to figure out most dominant parameters and/or parameter combinations. A major issue is always the so-called apparent diffusivity and the complementary ageing factor. Both these parameters have a large impact on the reliability of the chloride ingress predictions and with this, on the accuracy of the

service-life predictions of concrete structures. Back calculating the benchmark data would maybe enlighten the underlying mechanism that drives the change of the pore structure or pore morphology and its impact on the diffusivity. The way in which this happens in time is now controlled or, adjusted, with the ageing factor. Whenever this can be achieved, quantified and/or be related to a physical or chemical process, would be a major step forward. Relevant parameters involved in this process are those addressed in this paper.

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