NUMERICAL MODEL OF THE CHLORIDE TRANSPORT BY CAPILLARITY EFFECTS IN CEMENT MATERIALS

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Abstract: Corrosion that is induced by the presence of chloride ions in reinforced concrete structures is an important cause of premature degradation. This phenomenon has a high economic and ecological impact, especially near coastal areas and in countries where de-icing salts are used for road safety during winter periods. The transport of chloride ions in those materials is not only due to diffusion but also to the effects of water transport and capillarity mostly present with wet-dry cycles. These two last phenomena are currently very poorly modeled. A new system for the detection of free chloride ions in pore concrete was previously developed. It consists of a chemical sensor that undergoes fluorescent quenching in the presence of chlorides and optical fibers that transmit light and retrieve results. With this system, the presence of free chloride concentration as low as 350 mol/m³ in pore concrete solution can be detected without damaging the material. This work, therefore, aims to create a numerical model of multi-species and reactive transport of chloride ions by capillarity in a cementitious material. The model considers the diffusion of chloride ions and water transport by capillarity, as well as the chloride adsorption by the material with isotherms interaction. In a larger perspective, this study let to improve knowledge in concrete durability structures in severe environmental condition and the numerical model that can be created to predict their life service to better maintenance.

Keywords: Chloride, concrete, corrosion, fluorescence, modeling, optical fiber, spectroscopy, capillarity

1   INTRODUCTION

Many existing concrete structures worldwide are deteriorating. Surprisingly, many of these structures have been damaged only a few years after having been repaired (Vaysburd and Emmons 2001). The problem is particularly serious in reinforced concrete structures, where the effects of corrosion may compromise safety. The corrosion of rebar due to chlorides from de-icing salts (used for road safety and resulting from seawater in littoral zones) is the main cause of damage and early failure in reinforced concrete structures (Pruckner 2001; Qian and Cusson 2004). The expense involved in upgrading structures justifies innovations that support good decision-making for management, preventive maintenance, and repair (Cusson and Isgor 2004).

Therefore, for certain types of structures, the aim is to detect zones with premature deterioration risks and explore ways to assess their current performance and predict changes. Many methods exist for corrosion

detection and for chloride detection in reinforced concrete (McPadden 1996; Laferrière 2005). These methods can be described as destructive and non-destructive methods. The most destructive method commonly used is certainly the Soxhlet Method (ASTM C1524-02a). It can be applied when the aggregates contain a high background of naturally occurring chloride (ACI 222.1–96). Then, by pulverizing the sample to a fine powder or fine granular material, the test method C1152/C-1152M determines the acid-soluble chloride quantity and C1218/C-1218M determines the water-soluble chloride quantity. However, results with some aggregates have shown that the Soxhlet procedure extracts an extremely low amount of chloride, with most of it remaining in the rock, and therefore, it is not available for corrosion. On another hand, the non-destructive methods can provide a quantitative indication of the propagation of the corrosion (Tuutti 1982) but there is no precise indication of free chloride content in concrete pore water. Some non-destructive methods, as the half cell test (ASTM C876), can provide some information on the corrosion initiation but most of them suffer from drawbacks related to interpretation of results, electromagnetic interference and the time necessary for each test (Klinghoffer, Frølund, and Poulsen 2000).

Consequently, an in-situ, reversible and non-destructive method that monitors weak free-chloride concentrations in concrete is needed (Singh et al. 2000). Such a monitoring system would provide important support for modeling for preventive maintenance (Sorensen, Buhr, and Rostam 2002). These observations have justified the development of a new measurement system based on recent progress in optical fibers and chemical indicators. Over the past ten years, optical fibers have been mainly used for structural health monitoring to measure deformations, vibrations, and strains (Inaudi 1997; Glišić and Inaudi 2007; Rochette 2003). Those sensors are also employed in fields such as environment, space, automobile, medicine and biochemistry (Uwira, Opitz, and Lübbers 1984). The possibility to detect in-situ chemicals, in a reversible and non-invasive manner, has been demonstrated (Outhier 1997). Consequently, this technology has much potential to be adapted for monitoring invasive and harmful chemicals in concrete structures. This type of sensor is promising for corrosion monitoring because it offers attractive characteristics such as small size, flexibility, geometrical versatility, resistance to corrosive environments and, most importantly, that is a non-destructive method. Measurements using this new sensor provide accurate knowledge of chloride concentration at the steel rebar level, thus allowing new opportunities for comparisons with model predictions.

Two factors determine the chloride ions ingress in the cement materials : (i) the material characteristics, such as its permeability, its cover thickness and its components; and (ii) the microclimatic and boundary conditions at the concrete surface, as moisture, temperature and salt concentrations (David Conciatori, Denarié, and Brühwiler 2002). Simulations were hence carried out with the TransChlor prediction software (David Conciatori, Sadouki, and Brühwiler 2008). This numerical model considers temperature, carbonation, water transport, and chloride ionic transport. Moreover, TransChlor also considers the weather data (temperature, relative humidity, precipitations, etc.) and the presence of chemical products containing chloride by interaction isotherms (Luping and Nilsson 1993). The TransChlor model predicts temporal and spatial evolution of heat, carbon dioxide, liquid water, vapor and chlorides in concrete cover. As the water transport accelerate the corrosion initiation, this numerical model can also consider the capillary suction in the material porosity.

The main difficulty encountered in measuring capillary suction is the great complexity of obtaining experimental data. Indeed, with actual experimental methods, a capillary test only provides the chloride concentration according to the penetration depth at a given time. Then, it is necessary to carry out several tests under the same experimental conditions but of different durations to obtain the chloride evolution over time. The new chloride sensor inserted inside the cementitious matrix now allows measuring the evolution of the chloride concentration over time at a given penetration depth (David Conciatori, Laferrière, and Brühwiler 2010). This paper proposes to combine the advantages of two approaches: measurements taken from a new chloride detection system in concrete are compared with predictions of chloride macroscopic transport model.

2 EXPERIMENTAL WORKS

2.1 Material and characterization

A $3.38.10^{-3}$ m³ concrete cube (150x150x150mm) was cured according to a concrete mix design to average permeability (E/C = 0.52). Cement type CEM I 42.5 was used with a cement content of 375 kg/m³. The sample hence contains 1.27 kg of cement. The maximal diameter of the aggregate was 16 mm. The aggregate content and the density of hardened concrete value are respectively 1813 kg/m³ and 2384 kg/m³ and a water porosity of 12.99%. The curing was carried out in a climatic room for 31 days. The average temperature during this phase was 23°C (or 73.4°F) and the relative humidity was 33%. The class of concrete is C40/50 according to the European code designation (David Conciatori, Brühwiler, and Gysler 2010). The specific heat (c_T) and the thermal conductivity (λ_T) come from literature considering each component, aggregate, cement, and water (David Conciatori, Laferrière, and Brühwiler 2010). The vapor diffusion (D_h) has the value of 130.10^{-6} mm²/s. The liquid water transport factor (D_{cap}) depends on temperature and relative humidity of the pore solution and the chloride coefficient diffusion (D_{Cl}) value is $5.73.10^{-6}$ mm²/s (David Conciatori, Laferrière, and Brühwiler 2010).

2.2 Chloride sensor by optical fibers

The ion detection system consists of three functional elements: a sensor device which undergoes a transformation during measurements, a transducer which converts this modification into an optical signal, and a receiver that makes this signal interpretable by investigators (Boisdé and Harmer 1996). The generic term for a chemical sensor with the optical fibers used for transmission of light into and out of a detection zone is Optode (Sachs 1999). The fiber optic chemical sensor developed for this application is based on fluorescence spectroscopy measurements (Skoog and West 1997; Albani 2001). The light interacts with the matter (excitation state). Due to energy absorption, a molecule goes from a stable energy state to a higher unstable state (transient state). The molecule then returns to its original state through emission of energy to the medium in the form of light (luminescence) and heat. Fluorescence is thus the light emission corresponding to the energy jump from an excited state to the ground state. All molecules do not contribute to fluorescence. Deactivation processes may also reduce the lifetime of the excited state and if they are faster than light emission, fluorescence will not be observed. The fluorometric methods are of two types: direct methods based on the reaction of the analyte with a chelating agent to form a fluorescent complex; and indirect methods based on fluorescence quenching of a reagent caused by its reaction with the analyte. For anion detection such as chloride ions, we use the indirect method.

Fluorescence can be quenched (reduced in quantum yield or even eliminated) as the result of the interaction between the fluorophore (indicator dyes) and the species in solution (analytes). The fluorescence intensity observed then depends on the species concentration and is described by the Stern-Volmer's equation:

$$[1] \quad \frac{I_F^{(0)}}{I_F} = 1 + K_{SV}[Q]$$

with $I_F^{(0)}$ the fluorescence intensity without quencher, I_F the fluorescence intensity with quena cher, $[Q]$ the quencher concentration and K_{SV} the Stern-Volmer constant. Most substances cannot be visualized directly via luminescence spectroscopy; therefore indicators are added to the system to allow an indirect visualization of interesting species (Wolfbeis 2012). There exist many fluorescent molecules (fluorophores) with different excitation and emission wavelengths that can detect the presence of analytes (Probes 2001). After preliminary testing and upon review of environmental and biological studies (Biwersi, Tulk, and Verkman 1994; Oosthuizen et al. 1997; Huber et al. 2000), Lucigenin appeared to be the best indicator dye (Wissing and Smith 2000). In the form of a powder, Lucigenin was encapsulated at the end of an optode sensor. The material containing the Lucigenin powder is a Sol-gel because it is transparent and has a mechanical stability, a chemical inertia, and a flexible configuration. Moreover, the immobilization of the dye by encapsulation is simple and this is generally enough to prevent the leaching of the indicator (Lobnik and Čajlaković 2001).

The sensor design consists of an optical send-receive module which is composed of a light source (blue LED) coordinated with the excited wavelength of the indicator and a spectrometer (Figure 1a). Twelve multimode optical fibers connect the emission module to the optical probe (optode) (Mendoza, Lieberman, and Robinson 1997; Dybko et al. 1997). Under the action of the light signal emitted by the source, the transducer emits a fluorescence signal. This fluorescence signal is conveyed to the spectrometer by an offset fiber. The light signal is further converted into an electric signal and analyzed by digital electronic processing (Laptop). The miniaturization of the optode elements allows minimally invasive and in-situ implantation into the thickness of cover concrete. The use of optical fibers permits separation of sensor and spectrometer. All instrumentation elements are handy and easily transportable on site. The calibration curve (Figure 1b) with the Stern-Volmer's equation [1] was defined based on 250 calibration measurements (Laferrière et al. 2008). The $\frac{I_0}{I}$ linearity is verified from 30 mol/m³ (0.1%) to 350 mol/m³ (1.2%). The free chloride concentration in the pore solution of the concrete $[Cl_W^-]$ depends on the fluorescence intensity with I and without I_0 chloride ions:

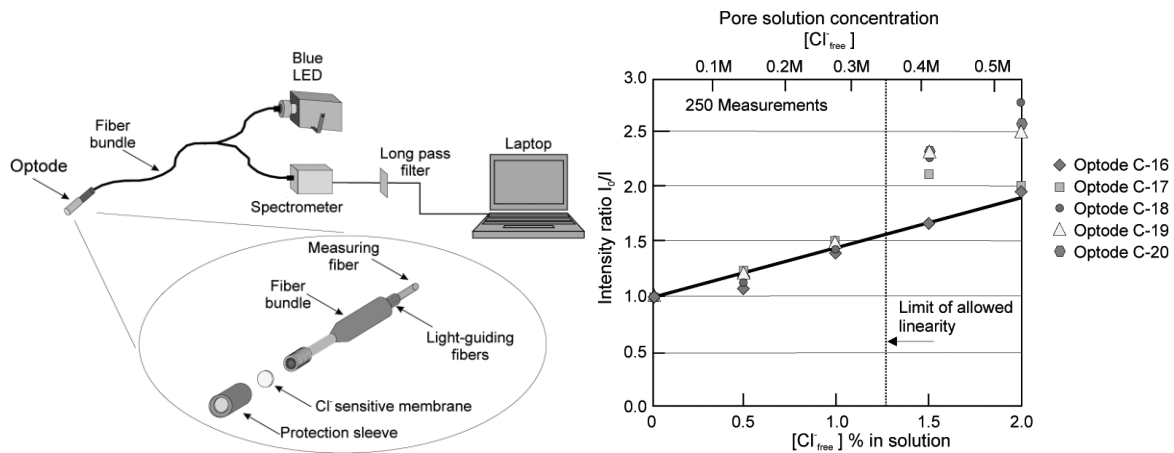$$[2] \quad [Cl_W^-] = 2.2306 \left(\frac{I_0}{I} - 1 \right)$$

Figure 1. (a) Instrumental setup and (b) Calibration of the sensor (Laferrière et al. 2008)

2.3 Capillarity test

The chloride sensor was placed during the mix 20 mm (0.787 in) from the bottom surface. The lower face of the sample was immersed in a solution of 513 mol/m³ NaCl (Figure 2a). In order to induce one-dimensional migration, the four sides of the sample were resin-coated, and the upper face remained in contact with the environment of the climatic room. During the test, temperature and relative humidity of the climatic chamber was maintained constant at 20°C (68°F) and 80% respectively. The fluorescence intensity measurements were taken every 15 minutes.

After approximately 7 hours of the test, the saline solution reached the optode and the chloride concentration began to increase (Figure 2b). The cure period, which lasted over 31 days in very low moisture conditions, caused an initial high effect of absorption when the cube was exposed to the saline solution at the test beginning. The saline solution was hence transported very quickly into concrete pores.

The maximum concentration was up to 350 mol/m³ after 32 hours, then slightly decreased to a value near 250 mol/m³ before slightly increasing again. The chloride concentrations measured were hence within the limit of the calibration (between 30 and 350 mol/m³) reflecting the reliability of the results (Figure 1b). With the material characteristic, the chloride quantity measured in the pore solution can be expressed in percentage of cement weight ($g_{Cl-}/100 g_{Cement}$) considering the sample volume, its porosity and its cement mass. The maximal quantity of chloride ions in the pore solution could not exceed 0.63% of cement weight since the chloride concentration at upstream was 513 mol/m³. This threshold value was reached at early

days. As the temperature and the moisture parameters do not vary during the experiment and external salt concentration was fixed, the free chloride concentration should gradually stabilize to 0.63% of cement weight. The increase of the chloride curve after 7 days highlights the equilibrium between the chloride concentration at upstream and in the pore solution.
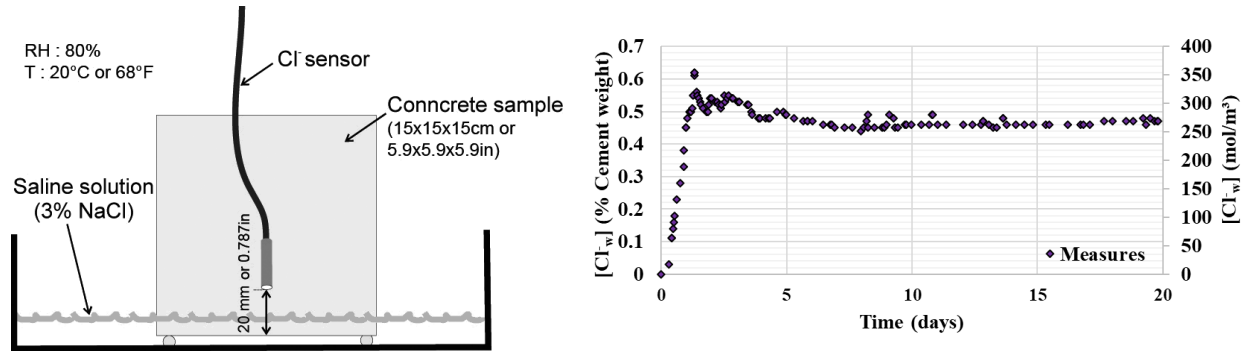

Figure 2. (a) Capillarity test schema and (b) Concentration evolution at 20 mm depth

3   NUMERICAL MODEL

TransChlor is a one-dimensional model intended for saturated and unsaturated concrete. It considers the thermal diffusion process, water transport by capillarity and water vapor diffusion as well as the carbonation evolution in order to simulate ionic chloride transport (Figure 3) (David Conciatori, Denarié, and Brühwiler 2002; David Conciatori, Sadouki, and Brühwiler 2008; Denarié, Conciatori, and Brühwiler 2003; David Conciatori 2006; David Conciatori, Laferrière, and Brühwiler 2010).
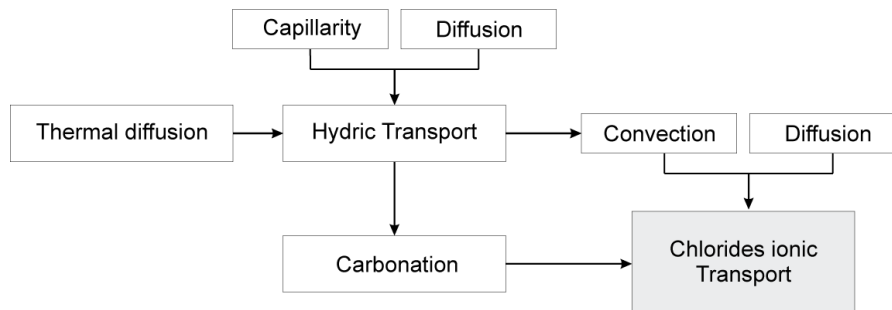

Figure 3. Schematization of transport model TransChlor

Chloride penetration in concrete is a slow and complex process involving many material and environmental variables. Some of these variables present significant random characteristics, thus a reliable prediction of long-term performance of concrete structures must consider the uncertainties related to these variables (Gharaibeh et al. 2000). The transport modes modeled by Fick's equations [3]-[6] are solved with a finite element method for spatial progression in the material and with a finite difference diffusion equation (implicit method) for the time progression. The thermal diffusion process considers the total specific heat (c_T) and total thermal conductivity (λ_T):

$$\frac{\partial T}{\partial t} = div\left(\frac{\lambda_T\left(T, w\right)}{c_T\left(w\right)} \cdot \overrightarrow{grad\left(T\right)} \right)$$

[3]

The total specific heat includes the specific heat of each concrete component (aggregates, water, and cement) and the influence of hydration heat. The total thermal conductivity varies according to the

temperature of concrete and the quantity of water (w) present (HAMFLER 1988). The hydrous transport: considers the vapor (D_h) and the contact with liquid water (D_{cap}):

$$[4] \quad \frac{\partial h_r}{\partial t} = \text{div}\left(D_h(T, h_r) \cdot \overrightarrow{\text{grad}(h_r)} \right) - \overrightarrow{D_{cap}}(t_{contact}, h_r, E/C, T) \circ \overrightarrow{\text{grad}(h_r)}$$

Hydrous transport depends upon the temperature (T) and the quantity of water present in the concrete (w) (Bažant and Najjar 1971). The effect of temperature is expressed with the Arrhenius' law. The liquid water transport is also determined by temperature (T) according to the W/C ratio, the relative humidity (h_r) and depends on the time of contact between concrete and liquid water. The capillarity coefficient D_{cap} decreases as a function of time representing the saturation of the material:

$$[5] \quad D_{cap} = D_{cap,t0} \cdot \left(\alpha_c + \frac{(1-\alpha_c)}{1+\left(\frac{1-t/10}{1+t_c}\right)^4} \right)$$

With the coefficient α_c and t_c obtained from experimental calibration on similar materials (Lunk and Mayer 1998). The CO_2 transport is not implicitly considered in TransChlor, however, the carbonation depth of concrete (x_c) is directly obtained thanks to the quantity of water, the CO_2 permeability of concrete, and the chemical rate of carbonation reaction (Papadakis, Fardis, and Vayenas 1991):

$$[6] \quad x_c = \sqrt{\frac{2 \cdot [CO_2] \cdot D_{e,CO2}}{[Ca(OH)_2] + 3 \cdot [CSH]}} \cdot \sqrt{t}$$

The external conditions are represented by the concentration of carbon dioxide $[CO_2]$. The rate of chemical reaction is calculated with the concentrations of calcium hydroxide $[Ca(OH)_2]$ and of calcium silicate hydrate gel [C-S-H]. The quantity of water and the concrete permeability are included in the diffusion coefficient of carbon dioxide ($D_{e,CO2}$). Finally, chloride transport includes the effects of their ionic diffusion in water (w) and the water movement (advection) [4] (D. Conciatori and Brühwiler 2006):

$$[7] \quad \frac{\partial C}{\partial t} = \text{div}\left(R_{Cl} \cdot c_f \cdot D_h \cdot \overrightarrow{\text{grad}(h_r)} + w(h_r, T) \cdot D_{Cl} \cdot \overrightarrow{\text{grad}(C)} \right) + R_{Cl} \cdot c_f \cdot \left(\overrightarrow{D_{cap}} \circ \overrightarrow{\text{grad}(h_r)} \right)$$

The chloride diffusion in the material is modeled by the diffusion coefficient (D_{Cl}). This coefficient varies according to temperature; however, in the absence of detailed test results, a constant diffusion coefficient is used. The delay of the chloride front compared to the water front during the advection movement is modelled by a delay coefficient (R_{Cl}) (Lunk and Mayer 1998). Cement pastes and carbonation rates (Lindvall, Andersen, and Nilsson 2001; Luping and Nilsson 1993; Tang and Nilsson 1996; Giffaut et al. 2014; Sugiyama, Ritthichauy, and Tsuji 2003; Ritthichauy et al. 2002) involves the adsorption of a varying amount of chloride ions. Thus, a distinction is made between the chloride ions attached to cement paste and free chloride ions moving in the concrete pore (c_f) using the Freundlich isotherm (Freundlich 1907). Modelling such complex physical and chemical effects leads to non-linear equations that are solved iteratively.

4   RESULTS AND COMPARISON

The comparison of the chloride profile at 20 mm with the TransChlor model predictions leads to several observations (Fig. 9). The chloride sensor measures and the model predictions both converge after 8 days of tests and this similarity continues thereafter. At the first 8 days, the trend of the chloride ion penetration front is similar. However, during this early period, the two curves differ for several hours. Faster initial migration measurements can have various causes. The delay coefficient included in the model (R_{Cl}= 0.7 in the present study) could be suspected, since this parameter is not known for this type of concrete. It can

also provide from the difference on the compaction of the sample: parameters used in TransChlor predictions are obtained from a concrete vibrated using a needle, whereas the cube sample compaction was carried out by vibration of the formwork in order to minimize risks of breaking the sensor. With small dimensions of the sample, it was difficult to introduce a vibrating needle. Therefore, the kinetic of the chloride penetration front is faster than in the model. In other terms, the concrete cube permeability seems to be higher than envisaged by the model. This front is also characterized by a more important peak of concentration is the pore solution corresponding to 0.6 % cement weight. This peak is the threshold chloride concentration in the pore solution and must be reached at steady state. After this peak, the free chloride concentration decreases up to the same value as TransChlor model curve. This phenomenon could be due to chemical reactions between the chloride ions and the sample solid phase which occurs after some delay. An adsorption of chloride into concrete could then explain a decreasing of free chloride concentration in the pore solution. As TransChlor considers interaction isotherms from the beginning of the test, the peak could not be visible but the adsorption rate in the model seems reliable as a good correlation is observed at lonthe g term. As the quantity adsorbed in the model is illimited, the numerical curve can not reach the maximal threshold of 0.6 % cement weight, however, after 8 days, the measures seem to slowly increase again maybe due to the limit of adsorption capacity of the material.
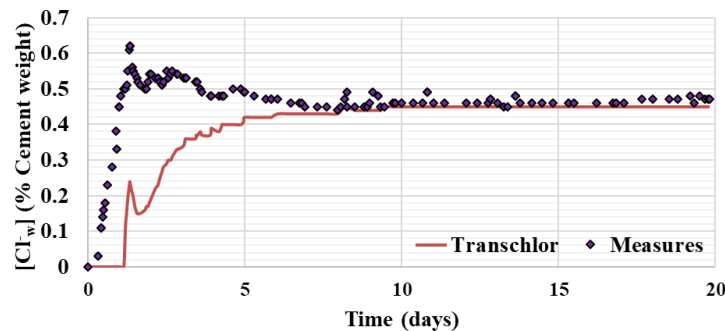

Figure 4. Comparison between TransChlor model and Chloride sensor measurements (Optode 20mm)

The capillarity tests reveal some weaknesses in the numerical model: some phenomenon is not simulated (variation of diffusion coefficient, the ratio between free and total chlorides, progressive micro-cracking, etc.). One may wonder if the capillarity suction equation [5] is well adapted for this kind of material and test: the water time exposition t_c could be under evaluated. The laboratory conditions as the sample's preparation variation (badly vibrated concrete), or intrusive elements (sensors) could also explain the differences observed between the measures and the TransChlor prediction. Indeed, the numerical model was rather developed for the simulation of realistic structural behavior and the considering of variable border conditions.

5   CONCLUSIONS

The goal of this research is to obtain reliable and reproducible information for early detection of chlorides and then to mitigate the damage through preventive maintenance. Model-measurement synergy is essential for sustainable development and cost control, including appropriate and timely planning of preventive measures. It is also important to well understand the chloride transport mechanisms in structures.

A new chloride sensor was previously developed allowing to measure the chloride concentration in the pore solution in a cement material by a non-destructive approach. The sensor could be used as remote monitoring of the bridge health for maintenance and can easily be placed and cast in the formwork. There is also no technological limitation to their number on structures. Optical fibers have long lifetimes, good mechanical and chemical resistance in concrete, no temperature effects, resilience to electromagnetic influences and finally, high data transfer capacities. The combination of monitoring with analytical simulation could improve the prediction of structural behavior without having to carry out destructive testing. The shape

of free chloride percentage front was well predicted using a numerical model as TransChlor despite a difference between values of prediction and measurement during the first few hours. It can be explained by the concrete heterogeneity and the delay coefficient used in the model. If the structural lifetime is considered, a few hours of initial differences can be neglected.

However, some limitations in the model, such as the considering of chemical reactions, can not allow to well understand the chloride behavior in the entire evolution. Further research will propose to simulate this capillarity test with a multi-species reactive transport model as PhreeqC (Parkhurst and Appelo 2012) in order to better understand the process which occurs.

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