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Numerical Strategy to Simulate Seawater Ingress in RC Concrete Blocks Exposed to Wetting-Drying Cycles in Field Conditions During 19 years

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Abstract. *Numerical results are compared to experimental data on concretes exposed in field conditions for 19 years and subjected to wetting/drying cycles in seawater after a couple of curing days. They were obtained thanks to a hydration model assuming fully hydrated concretes (19 years of curing time) and a reactive transport model in saturated conditions taking into account precipitation/dissolution of minerals and their kinetics and adsorption of ionic species on C-S-H. Numerical results show surprisingly rather good results, especially for concretes with fly ash. For OPC, although model considers average bulk porosity modifications, the experimental apparent diffusion coefficient increases much more. For concretes with silica fume, numerical results also show underestimations of total chloride content also experimental apparent diffusion coefficients are constant. Analysis of hydration calculations show that concretes are not fully hydrated after 19 years. Additional chloride content from reactions between anhydrous phases and chloride ingress may appear.*

Keywords: *Concrete, Chloride Binding, Seawater, Long-Term Exposure, Field Condition.*

1 Introduction

Numerical study of reinforced concrete durability exposed to seawater in field conditions is difficult in several aspects. Environmental conditions can play a significant role in the chloride ingress (temperature, RH, wetting-drying cycles, orientation, wind). Curing time is also important because of possible interactions between concrete and seawater as well as initial presence of chloride in mixing water (Suryavanshi and Swamy, 1996; Caré, 2008 to cite a few). Previously reactive transport model taking into account precipitation and dissolution of mineral species with their kinetics as well as adsorption of ionic species on C-S-H were successfully used in order to simulate chloride ingress in laboratory concrete specimens (fully hydrated, controlled exposure conditions, saturated conditions) (Tran *et al.*, 2018). However, in field conditions, concrete is not fully hydrated when they are exposed to seawater. Influence of hydration degree on chloride binding capacity of concrete is interesting.

Numerical simulations were done and compared to experimental data on concretes exposed in field conditions for 19 years and subjected to wetting/drying cycles in seawater after a couple of curing days. A hydration model following by a reactive transport model taking into account precipitation/dissolution of mineral species with their kinetics as well as adsorption of ionic species on C-S-H were used. Regarding all the phenomena to take into account, severe hypotheses were done such as saturated materials and 19 curing years. The aim of this study is

to identify if such a severe hypothesis is sufficient in order to give a good approximation of chloride ingress.

2 Experimental Study and Numerical Approach

2.1 Experimental Study

Several concretes from the French project BHP2000 are exposed to sea- water and wetting-drying cycles in La Rochelle harbor (western French coast) since 19 years after 1 curing day (Baroghel-Bouny *et al.*, 2013). 4 HPCs with or without silica fume (SF) and 3 normal-strength FA concretes which can appear as interesting mixtures with respect to current sustainable-development considerations were studied. All concretes described in this article were casted with the same cement (CEM I 52.5 PM ES CP2, see Table 1). Concrete mix-design are described in Table 2.

Table 1. Chemical and mineralogical composition of the binder (%).

| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | K ₂ O | Na ₂ O |
|-------------|------------------|--------------------------------|--------------------------------|-------|------|-----------------|------------------|-------------------|
| CEMI | 21.39 | 3.49 | 4.16 | 65.12 | 0.82 | 2.86 | 0.30 | 0.12 |
| Fly Ash | 55.86 | 25.40 | 6.05 | 1.83 | 0.63 | 0.11 | 4.77 | 0.24 |
| Silica Fume | 94.75 | 0.07 | 0.08 | 0.34 | 0.28 | 0.05 | 0.28 | 0.18 |

Table 2. Mix-design, along with average 28 days cylinder compressive strength and 90 days porosity accessible to water (measured after water curing).

| Concrete | Gravel/sand | Cement | FA | SF | Water | W/binder | σ_c | Porosity |
|----------|-------------|--------|----|----|-------|----------|------------|----------|
| M25FA | 992/905 | 195 | 48 | - | 187 | 0.77 | 23.5 | 0.157 |
| M30FA | 986/879 | 223 | 95 | - | 166 | 0.52 | 48.5 | 0.141 |
| M50FA | 956/809 | 325 | 79 | - | 181 | 0.45 | 53.0 | 0.150 |
| M50 | 937/806 | 410 | - | - | 197 | 0.48 | 55.5 | 0.145 |
| M75 | 1025/808 | 461 | - | - | 146 | 0.32 | 75.0 | 0.114 |
| M75SF | 1044/877 | 360 | - | 22 | 136 | 0.36 | 85.5 | 0.100 |
| M100SF | 1049/871 | 377 | - | 38 | 124 | 0.30 | 109.0 | 0.084 |

3.2 Numerical Approach

A physically and chemically based model was developed to simulate ionic ingress in the materials. Calculations are managed with TOUGHREACT software (Xu *et al.*, 2012). The chemical part uses the thermodynamical database Cemdata18 (Lothenbach *et al.*, 2019). Hydration and interstitial solution calculations precede this reactive transport simulation (see Figure 1 for the description of the simulation steps). Input data are limited to chemical and mineralogical composition of the binder, concrete mix-design, average bulk porosity and effective diffusion coefficient of concrete.

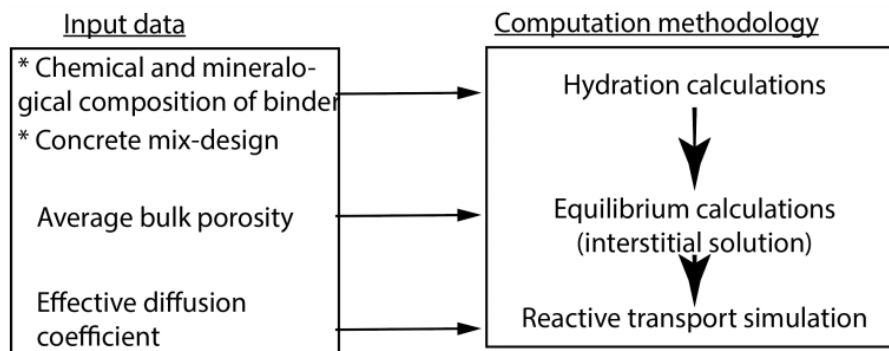


Figure 1. Flow chart of the reactive transport model.

The reactive transport model considers precipitation and dissolution of mineral species and their kinetics and adsorption of several ionic species on C-S-H (Cl^- , Na^+ , K^+ , Ca^{2+} , SO_4^{2-}). It has been validated on different experimental data such as laboratory concretes exposed to different solutions containing chloride (Tran *et al.*, 2018). Nevertheless, ingress of seawater in concrete exposed to field conditions after only few curing days is a difficult subject. In the case studied here, hydration was not complete when concretes were exposed to seawater leading to interactions between ionic species contained in seawater and anhydrous phases.

Although concretes are exposed to wetting-drying cycles, the present numerical model assumes that concrete is saturated by adopting a pure fickian approach (see Equation below). In fact, the wetting-drying cycle period is short (12 hours) and the mean value of the relative humidity in La Rochelle harbor is high (close to 67% (Baroghel-Bouny *et al.*, 2013)). Except for the first millimeters where carbonation can occur, this hypothesis seems to be reasonable (Soive *et al.*, 2018).

$$\frac{\partial \phi c_j}{\partial t} = \text{div} \left(D_e \vec{\nabla} c_j \right) + q_j \quad (1)$$

where ϕ is the average bulk porosity, c_j the concentration of species j [mol.m^{-3} of solution], D_e the effective diffusion coefficient [$\text{m}^2.\text{s}^{-1}$] (supposed to be equal for all species) and q_j source or sink term [$\text{mol.m}^{-3}.\text{s}^{-1}$]. Ions can chemically react with the matrix to precipitate minerals (*e.g.* ettringite, brucite, Kuzel and Friedel's salts) or to dissolve others (portlandite, monosulfate). They also can be bound (adsorbed or absorbed) to the surface of the matrix. As described in previous studies (Baroghel-Bouny *et al.*, 2013; Soive *et al.*, 2018), all mineral precipitation/dissolution kinetics also need to be taken into account. In addition, the effective diffusion coefficient D_e can evolve with average bulk porosity value change as follows:

$$D_e = \phi \tau D_w \quad (2)$$

where τ and D_w are the tortuosity and the diffusion coefficient of ionic species in water.

A 1D diffusion model is adopted. 250 elements are used to simulate ionic species ingress in 10cm structural depth. By sake of simplicity and to avoid complex calculations of ionic species ingress during hydration, hydration duration is supposed to be equal to the greater exposition duration (19 years). Of course, this is a very first approximation owing to the competition between hydration and seawater ingress at first time exposure. Chemical reactions between seawater and anhydrous species are not considered.

4 Results and Discussion

Total chloride content profiles were measured after 2, 4, 10, 16 and 19 years of exposure. Comparison between experimental data and numerical results with 19 curing years is exposed in Figure 2. Knowing the limited number of input data and the difficulty to catch all the phenomena, the numerical simulations show hopeful results.

Three aspects can be underlined: the ‘‘convection zone’’, the evolution of apparent diffusion coefficient as a function of time and possible chemical reactions between chloride and anhydrous phases.

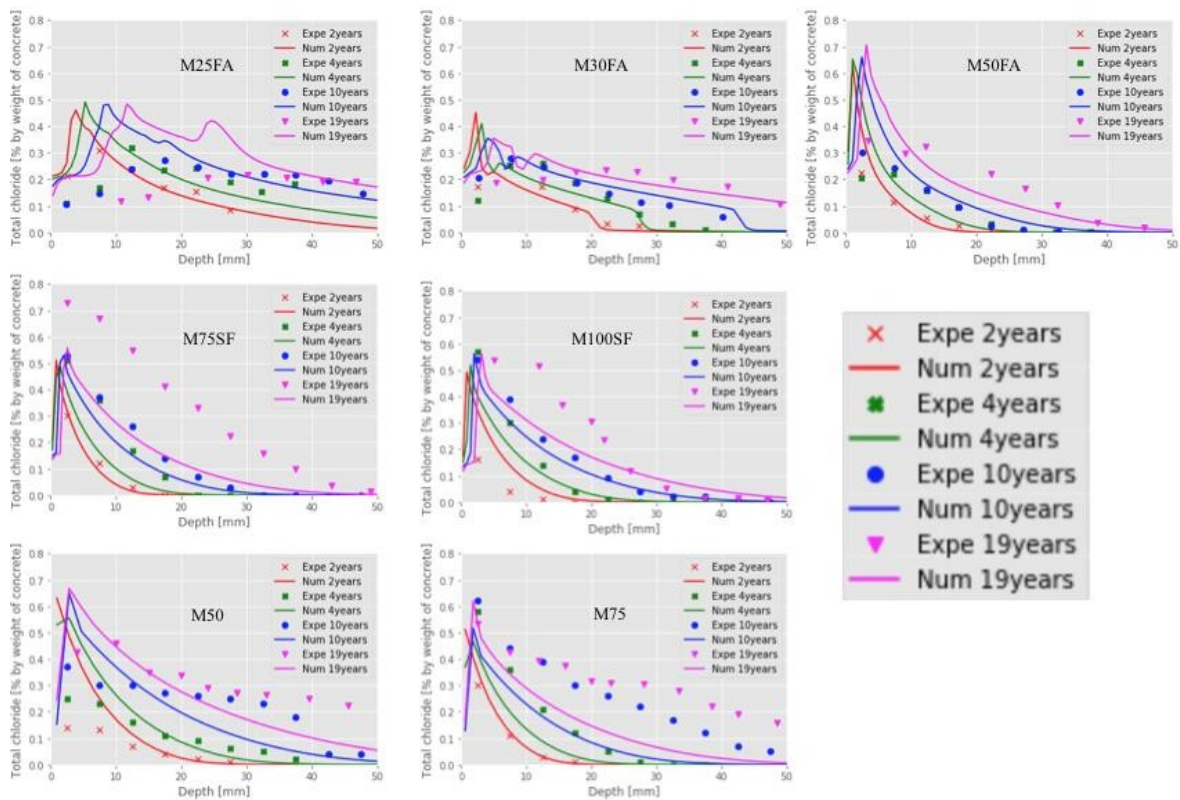


Figure 2. Comparison between experimental data and numerical results for total chloride profiles for 2, 4, 10, 16 and 20 years of exposure (19 curing years).

4.1 The « Convection Zone »

For concretes with fly ash (M25FA, M30FA, M50FA), results are rather good except in the first millimeters and although numerical model does not consider wetting/drying cycles. The depth at which total chloride content is maximum is to underline. This zone is often associated with the “convection zone”. Nevertheless, even with a model that simulate the ingress of ionic species in saturated concrete such as the present one, this phenomenon is observed. As reported by Jakobsen *et al.* (2016), chemical and mineral zonation appear. Three zones (magnesium, sulfur and chloride-rich zones) are found irrespective of the age, location or binder composition. Figure 3 show that the model can qualitatively simulate these zones. However, in this “convection zone”, results are very different from experimental data. The use of a model considering wetting-drying cycles is necessary in order to catch phenomena in this zone (convection, local chloride concentration increase).

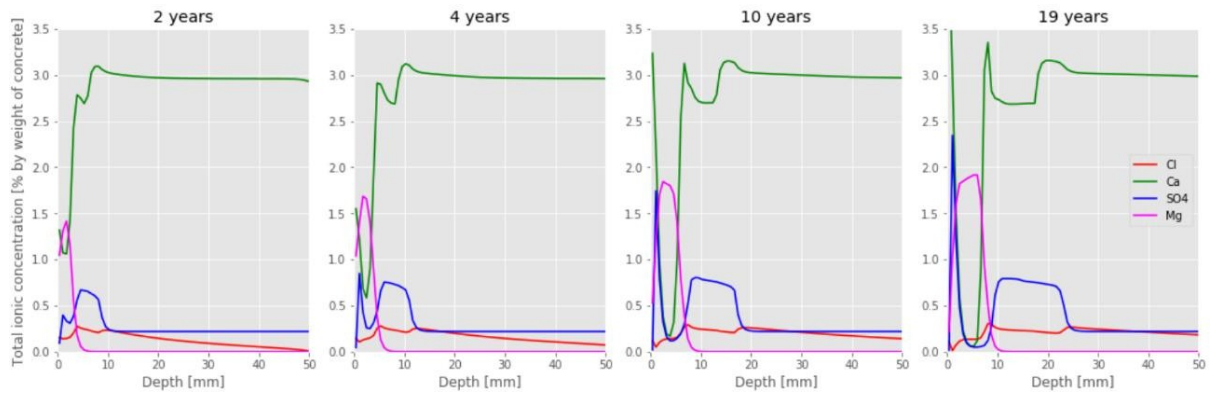


Figure 3. Ionic species ingress after 2, 4, 10, 16 and 20 years of exposure for M25FA (19 curing years)

4.2 The Evolution of Apparent Diffusion Coefficient with Time

For OPC (M50, M75), whereas profiles are close to experimental data after 2-year exposure, total chloride contents are underestimated for greater exposure durations. These differences can be partly explained by the fact that apparent diffusion coefficient (which includes both effective diffusion and binding) for M50 and M75 increases with time (by inverse analysis calculations on experimental data) from $1.6 \cdot 10^{-13}$ to $2 \cdot 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ and $3.6 \cdot 10^{-13}$ to $1.6 \cdot 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$, respectively (see Figure 4). The present model considers microstructure evolution (average bulk porosity) due to mineral dissolution or precipitation (see Equation 2). It is also able to compute the evolution of chloride binding. However, the apparent coefficient increase is much greater than the one computed. Deeper experimental data investigations must be done in order to determine if other phenomena that are not modeled can appear, such as cracks, properties differences between concrete first millimeters and deeper.

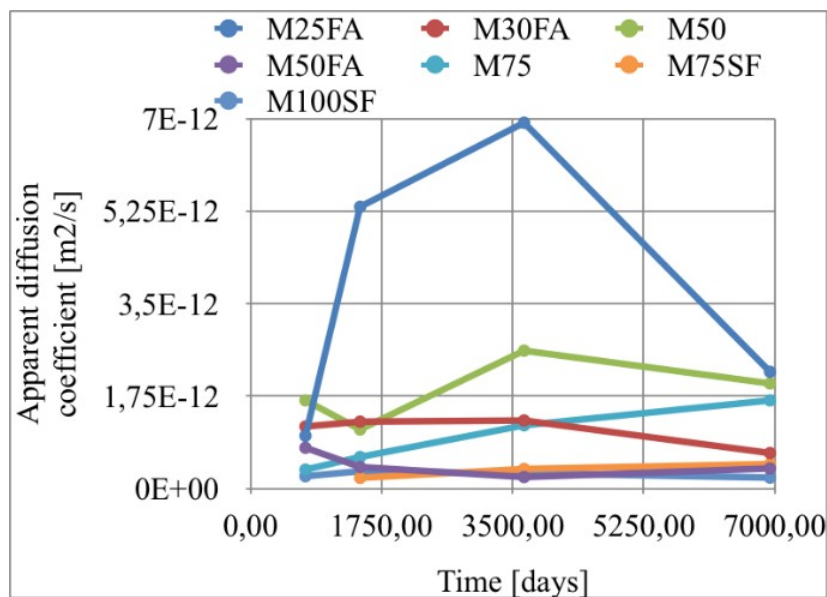


Figure 4. Apparent diffusion coefficient calculations by inverse analysis.

4.3 Possible Chemical Reactions between Chloride and Anhydrous Phases

For concretes with silica fume (M75SF, M100SF), underestimations appear after 2-year exposure. Nevertheless, as can be seen in Figure 4 and contrary to M50 and M75, the apparent diffusion coefficients are constant. By analyzing hydration results of M75SF thanks to a hydration model developed at Cerema (Lavergne *et al.*, 2018) (see Figure 5), results show that anhydrous phases are still present after 19 curing years (6500 days) as well as a lack of monosulfate. These results confirm that hydration is slower for these concretes. However, presence of seawater can affect the hydration process by accelerating hydration or precipitating minerals containing chloride (Friedel's salt) (Li *et al.*, 2018). Unfortunately, the present model is not able to calculate chloride ingress in concretes that continue to hydrate.

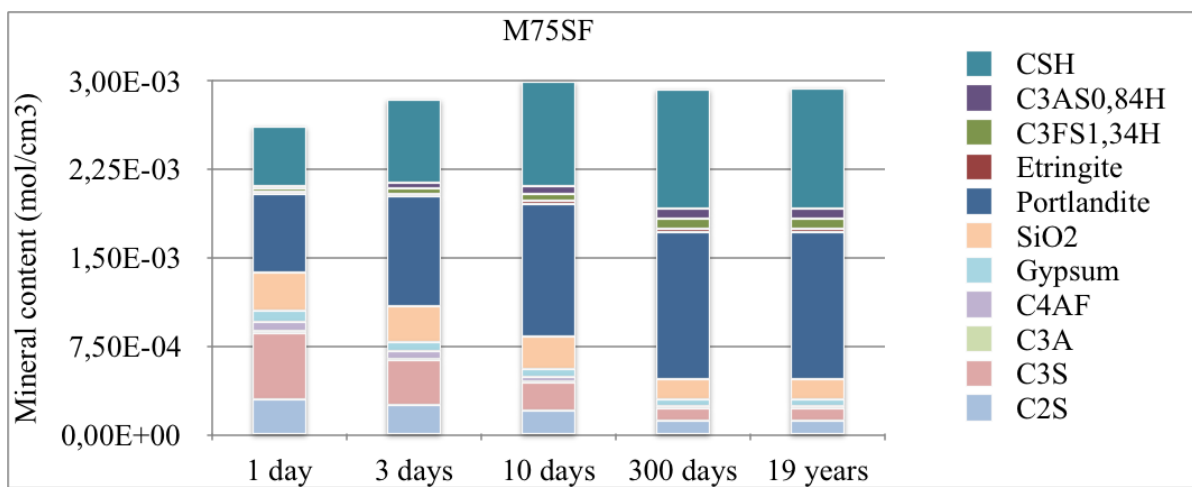


Figure 5. Hydration results after 1, 3, 10, 300 and 6500 curing days.

5 Conclusion

Experimental data on concretes exposed to tidal zone in field conditions for 19 years and subjected to wetting-drying cycles in seawater after a couple of curing days were compared to numerical results. Two OPCs, three concretes with fly ash and two concretes with silica fume with the same cement were studied. The numerical results were obtained thanks to a hydration model and a reactive transport model considering precipitation/dissolution of minerals and their kinetics and adsorption of ionic species on C-S-H.

A pure fickian approach in saturated materials is assumed. In addition, due to difficulties to model interactions between ingress of ionic species and hydration, numerical model assumes that hydration lasts for 19 years (last measurement value).

Knowing the limited number of input data and the difficulty to catch all the phenomena, the numerical simulations show hopeful results, especially for concrete with fly ash. In addition, the model can qualitatively simulate chemical and mineral zonation (magnesium, sulfur and chloride-rich zones) as reported in the literature. For OPC and concretes with silica fume, numerical results underestimate chloride content. For OPC, although numerical model considers porosity change due to mineral precipitation/dissolution, it is not able to simulate increase of apparent diffusion coefficient as observed on experimental data. Further investigations must be done in order to observe if cracks are visible. For concretes with silica fume, underestimation cannot be fully explained yet. One explanation can be the lack of additional chloride content coming from reactions between chloride and remaining anhydrous phases. Indeed, by analyzing results of hydration calculations, results show that anhydrous phases are still present even after 19 years and that additional chloride content can exist.

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