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Requirements and possible simplifications for multi-ionic transport models – Case of concrete subjected to wetting-drying cycles in marine environment

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HIGHLIGHTS

- A physically and chemically based model was used to simulate chloride ingress.
- The use of precipitation/dissolution kinetics is essential.
- "Intrinsic" permeability value do not play a significant role on the chloride ingress.
- Boundary layer thickness that reflects the evaporation kinetics is not important.
- Simulations carried out in saturated conditions provide good results.
- Results have to be further discussed for higher "intrinsic" permeability values.
- Simulations with different wetting drying cycles frequencies have to be performed.

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ABSTRACT

In this paper, a physically and chemically based model, which describes coupled ion-moisture transport, is used to simulate chloride ingress in concrete elements subjected to wetting-drying cycles in marine environment. Various assumptions are tested, in order to quantify the influence of taking into account dissolution/precipitation kinetics or to underline the differences between complex model and very simple one assuming saturated conditions in the latter case. Numerical simulations are compared to experimental chloride concentration profiles. Experimental data were obtained on OPC concrete (w/c = 0.43) specimens exposed to 6 h/6 h seawater wetting-drying cycles in lab (where RH and T are controlled).

The results show that when the initial amounts of hydration products are known, the assessment of the chloride binding parameters is not needed. In addition, including reaction kinetics in the model is essential and improves the predictions compared to a pure thermodynamical approach. Moreover, according to sensitivity analysis the boundary layer thickness that reflects the evaporation kinetics and the "intrinsic" permeability are not important parameters for the studied concrete. Updating at each time step the transport properties in order to account for dissolution/ precipitation of mineral species does not change very much the chloride content profiles as well. Furthermore, simulations carried out in saturated conditions provide similar results to those obtained when accounting for wetting-drying cycles for the studied concrete. Then, it may be possible to use a simpler model (ie saturated conditions), and thus avoid the problematic assessment of the "intrinsic" permeability, to predict the service life of a RC structure cast with the concrete studied.

1. Introduction

The main deterioration cause for reinforced concrete structures exposed to marine environment is the corrosion induced by chloride penetration into concrete. Owing to the expensive costs of

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repair and maintenance it is highly requested to develop reliable models intended to predict the chloride concentration profiles in tidal zone where the corrosion is occurring faster than in the other zones in the structure [1–3].

Many studies have been dedicated to the modeling of chloride transport through unsaturated concrete by taking into account diffusion and convection. Some are based on an approach that describes moisture ingress as a pure fickian process [4–8]. Others are coupled moisture-multionic transport models that take into account advection and diffusion process for liquid and gas ([6,9] to cite a few). However, these models have several limitations. First, they cannot be applied to all types of concrete since they use empirical relationship for the chloride binding isotherm. Few models take into account both Friedel's salt precipitation and "physical" binding onto C-S-H [10,9] but they do not have been used with seawater. Second, pH calculation is often missing. However, the aim of chloride transport modelling is to lead to a better understanding of the mechanisms and to a better estimation of the time needed to reach a given critical or threshold value, which induces depassivation, at the first layer of reinforcement. Several threshold expressions proposed in the literature need the hydroxyde concentration [11,12]. Then chloride ion propagation models involve the evolution of the pH in the cementitious material.

Furthermore, transport in unsaturated concrete involves many complex mechanisms. The number of parameters that describes the various phenomena involved can be significant. The modelling requires taking into account the transport of liquid water and that of the gas phase (dry air and water vapour), and the transport of the ions contained in seawater. With regard to moisture transport, a number of studies have been performed on the drying process and how to model it [13–16]. They show that, in addition to water vapour sorption isotherm and to the conventional parameters related to transport ("intrinsic" permeability, and water vapour diffusion coefficient), it is necessary to estimate an evaporation layer thickness over which diffusion occurs [17].

Faced to this situation, the main objectives of the study described in this paper is to evaluate the influence of several parameters in order to identify possible simplifications and requirements for transport models in concrete subjected to wetting-drying cycles in marine environment. In particular, the study aims at showing if a hypothesis of fully saturated concrete is correct when modelling realistic 6 h/6 h drying-wetting cycles with respect to field conditions. A numerical simulation program for chemically reactive non-isothermal flows of multiphase fluids in porous and fractured media [18], has been used. The main advantage of using this type of model is to reduce the number of empirical parameters associated with chloride ions bound onto concrete during seawater ingress. In addition, it allows to predict mineral precipitation/dissolution and the pH evolution. The influence of mineral precipitation/dissolution kinetics and of several parameters and procedures is then evaluated, as the "intrinsic" permeability, the evaporation layer thickness, updating porosity and "intrinsic" permeability. The numerical results have been compared to experimental data measured on concrete samples subjected to wetting-drying cycles with seawater in lab. The differences between a complex model and a very simple one (based on a reactive transport model and assuming saturated conditions) are also evaluated.

Section 2.2 describes the experimental set-up used for exposing concrete specimens to wetting-drying cycles with natural seawater and controlled environmental conditions. Section 3 depicts the governing equations used to simulate moisture and ionic transport in non-saturated cementitious materials. Section 4 deals with the input data and the hypothesis adopted. Section 5 shows the predicted and experimental total and water soluble (free) chloride concentration profiles.

2. Experimental study

2.1. Concrete mixtures

The experimental study was carried out on normal-strength OPC concrete (BO) submitted to wetting/drying cycles with seawater in lab. The mix proportions of this concrete are summarized in Table 1. The aggregates are composed of limestone gravel and calcareous and silico-calcareous sand. The cement is a CEM I 52.5 PM ES CP2 type, according to the European standard. The mix-design principles of this concrete are explained in [19].

2.2. Experimental procedure

The BO concrete was cast in cylindrical specimens (thickness $= 100 \pm 1$ mm; diameter $= 110$ mm). After demoulding, the non-curved surfaces were polished to have plane and clean surfaces. The specimens were immersed into water during 1.5 years. Then, a dense epoxy coating was applied to lateral surface and one plane surface, leaving an exposed plane surface to ensure a one-dimensional flow inside the cylinders.

The samples were submitted to 72-h vacuum saturation with a 0.1 N NaOH solution prior to exposure to wetting and drying cycles. This presaturation ensures that the pH remains greater than 13, a value that is close to that of the concrete pore solution before ingress of aggressive solution. Each specimen was exposed to 2 daily cycles of 6 h of seawater penetration (seawater extracted from the bay of Saint-Brieuc in northern France) and drying for 6 h. During drying, a fan is used to ensure a well-mixed atmosphere in the chamber. BO samples were exposed to these conditions during 90 and 180 days. Temperature ($T = 20 \pm 1^{\circ}C$) and relative humidity ($RH = 65 \pm 5\%$) were controlled thanks to an air-conditioning system.

2.3. Measurements

Total and free chloride concentration profiles have been measured on cores at given depths. A Profile Grinder was used to extract powder ($< 80\mu m$) from the samples over a 50 mm disk and allows a 2 mm penetration increment. The total chloride concentration (respectively free chloride concentration) has been assessed by means of nitric acid (respectively water) extraction and potentiometric titration (by using a $0.01N\ AgNO_3$ solution), according to the AFPC-AFREM procedure [20].

3. Modelling approach

A physically and chemically based model, which describes coupled ion-moisture transport, is used to simulate chloride ingress in concrete elements subjected to wetting-drying cycles in marine

Table 1
BO concrete mix-design [19].

Concrete	Limestone gravel 4/20 ($kg \cdot m^{-3}$)	Calcareous and silico-calcareous sand 0/5 ($kg \cdot m^{-3}$)	Cement CEMI 52.5 ($kg \cdot m^{-3}$)	Water ($kg \cdot m^{-3}$)	w/c
BO	1192	744	353	152	0.43