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Marinelle El Khoury, Frederic Grondin, Emmanuel Rozière, Rachid Cortas, Fadi Hage Chehade. A non-linear multi-scales chemo-mechanical model describing the delayed evolution of concrete structures in marine environments. 25e Congrès Français de Mécanique, Nantes, 29 août-2 septembre 2022, Association française de mécanique, Aug 2022, Nantes, France. hal-04280106

HAL Id: hal-04280106

<https://hal.science/hal-04280106>

Submitted on 10 Nov 2023

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A non-linear multiscale chemo-mechanical model describing the delayed evolution of concrete structures in marine environments

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Abstract: (16 gras)

The failure of offshore structures is a major issue as they lead to economic, environmental, and social disasters. Assessing the durability and long-term behavior of these structures subjected to chemical and mechanical degradation is subsequently vitally important. The analysis of these coupled phenomena induced by seawater attack and mechanical loading is complex and requires the development of innovative measurement systems and modelling strategies. Hence, multiscale protocols, starting from the microscopic scale of the cement paste, seems relevant for the characterization of the chemo-mechanical behavior of offshore structures. Therefore, the competition between protective layers' formations and harmful effects of seawater ions has been coupled with the creep phenomenon.

Keywords: Cement, chemo-mechanical, degradation, multi-scale, seawater.

1 Introduction

Controlling the environmental conditions of concrete structures is almost impossible. Therefore, it should be considered as a given parameter in a durability study. While implementing durability assessment protocols, it is essential to get as close as possible to the real conditions to obtain representative results.

Sea water exposure is critical due to its complex composition and the multiple phenomena induced by the seawater ions [1], [2]. Previous studies have focused on sulfate attack characterization [3] and on chloride diffusion [4]. But at the same sulfate concentrations, seawater is different from sulfate attack [5]. Given the competition between the protective and expansive effects [6], [7], it seems interesting to represent seawater as a combination of all the anions and cations present in the seawater during its reformulation in the laboratory.

The chemo-mechanical coupling between calcium leaching and mechanical damage of cementitious materials has been studied by [8]–[11]. It shows a strong coupling between calcium leaching and mechanical behavior: as leaching increases, a loss of stiffness and strength has been experimentally observed [11]. But leached concrete becomes more ductile during chemical degradation [11], [12]. The coupling between creep and leaching of concrete has been studied in [12]–[14]. It was seen that

the deformation in the combined test accelerates and reaches tertiary creep [13]. This demonstrates the effect of long time loading combined with leaching.

The strong coupling of chemical degradation with mechanical effects has been very little studied at the levels of modeling and experimentation. It is also noteworthy that no study has associated the creep phenomenon to the seawater attack.

To study the chemo-mechanical coupling, a new multiscale numerical and experimental approach will be proposed in this study. The paper focuses on the combined effects of hydration associated with seawater attack, and their effects on the creep and mechanical performance of offshore structures by considering all the ions present in the marine environment.

2 Multiscale chemo-mechanical protocol

At the mortar scale, the material is assumed to be made of two continuous media: the cement paste, considered in this case as homogeneous, and the sand particles. The simulation of the chemo-mechanical coupling proposed in this work considers a mechanical calculation on a material whose microstructure has evolved chemically and where damage and viscoelastic behavior are coupled.

For this purpose, a coupling between two codes has been realized: CemPP [15], for the simulation of hydration and chemical reactions at the cement paste scale (model coupling hydration to seawater attack), and the finite element code Cast3M for the simulation of the mechanical behavior, loss or gain of elastic properties defining consequently the mechanical strength of the structure (mechanical damage model based on [16], [17] (Eq.1-2), as well as creep using 4 chains of Kelvin Voigt (Eq.3). The cement paste represents a heterogeneous material composed from multiple phases of anhydrous cement and hydration products. Mechanical properties of the cement hydrate phases have been gathered from literature and are summarized in the work of [18]. The damage model adopted for the cementitious phases is the one developed by Fichant et al. [16], [17]. A strong assumption was made in the creep model: All phases except C-S-H have a negligible viscoelastic behavior compared to C-S-H. The total stress σ is calculated from the effective stress (Eq.1), and the viscoelastic strain tensor is calculated according to the creep compliance $J(t)$ using 4 chains of Kelvin Voigt (Eq.2-3):

$$\sigma = (1 - D) C^0 : \varepsilon^e = (1 - D) C^0 : (\varepsilon^T - \varepsilon^v) \quad (\text{Eq.1})$$

$$\varepsilon^v = J(t) \otimes \sigma \quad (\text{Eq.2})$$

Where D is the scalar damage variable, C^0 represents the undamaged stiffness tensor and ε^e the elastic strain field. The creep compliance function is defined as:

$$J(t) = \sum_{i=1}^n \frac{1}{\kappa_i} \left(1 - e^{-\frac{\kappa_i}{\tau_i} t} \right) \quad (\text{Eq.3})$$

Where τ_i represents the characteristic times of the Kelvin-Voigt chains: $\tau_1=0.1$ day, $\tau_2= 1$ day, $\tau_3=10$ days, and $\tau_4=100$ days, and κ_i the elementary phase stiffness.

After defining the mechanical behavior of the cement paste, a homogenization method was designed to assess the properties of the mortar. At the mortar scale, the creep-damage model requires the following input parameters: Young's modulus, Poisson's coefficient, strength, rigidity, density, fracture energy and creep coefficients (Elementary rigidity). The start of cement exposure is 3 days. The algorithm used at a time of calculation "ti" is summarized in Fig. 1.

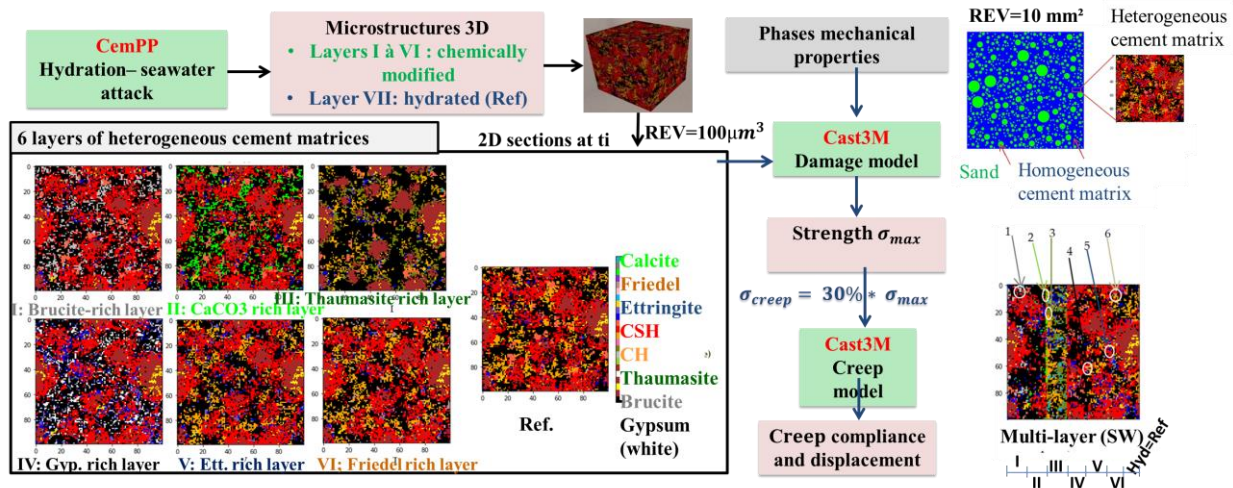


Fig. 1 : Multi-scales chemo mechanical modelling

First of all, using the chemical reactions defined in CEMHYD3D, the simulation of hydration is performed by cycles of dissolution, diffusion, and precipitation.

Secondly, since the chemical action of seawater must be described as one of many reactions taking place simultaneously [19], and since the chemical reaction time has been assumed to be much faster than diffusion, seawater attack results in layers corresponding to the different fronts of dissolution/precipitation. The characteristic size of the microstructure being very small, a total replacement of the cement phases by their reaction product is adopted. Each layer represents ionic / chemical attack and product formation. To understand fully the effect of each phase formed or transformed on the mechanical behavior of the structure, each layer is simulated separately as a material under hydration-chemical reaction coupling. Then, the multilayer modified microstructure named “SW” is compared to the hydrated intact one named “Ref” (Fig.1). The simulation of the hydration-seawater attack coupling process was carried out on $100\mu\text{m}^3$ cement paste using CemPP and 10 mm^2 for mortar using Cast3M.

To validate the model, experimental tests were performed.

Mortar cylinders have been prepared using a water to cement (W/C) ratio of 0.6 and OPC cement. Cement paste cylinders have been prepared with $W/C=0.5$. At the age of 3 days some specimens were immersed in tap water (“Ref.”) and other in a laboratory reconstituted seawater (“SW”). For diffusion acceleration purposes a $W/C=0.6$ and salinity of 70 g/L (equivalent to the double of reference seawater [20]) were considered. Epoxy resin layers were also applied at the two surface ends to ensure 2D diffusion.

The experimental protocol proposed in Fig.2 allows analyzing the effect of seawater attack on cementitious materials. This analysis is carried out at the macroscopic scale (variation of mass, volume and length) by including mechanical criteria (estimation of strength and stiffness). At the microscopic scale, the characterization allows to identify the formed and transformed phases using cement pastes samples. To include long time loadings in our study, a new creep rig has been implemented (Fig.2).

The experimental characterization presents the originality of considering all the ions present in the seawater solution.

The experimental protocol proposed allows analyzing the attack of seawater on cementitious materials. This analysis is carried out at the macroscopic scale (mass, volume and length variations) by including mechanical criteria (strength, stiffness and creep evolutions). At the microscopic scale, the characterization allows to identify the formed and transformed phases. This microscopic characterization takes into account the all the ions present in the salt solution.

Thus, distinguishing the effects of the ions and their effects on the microstructure and the overall mechanical behavior of the structure is experimentally exhaustive. Moreover, the attack of seawater is slow, so that to reach advanced degrees of degradation, it takes several years. Thus, the use of reliable

numerical models is essential to model the effect of each ion on the microstructure and to represent the chemo-mechanical phenomena over long periods.

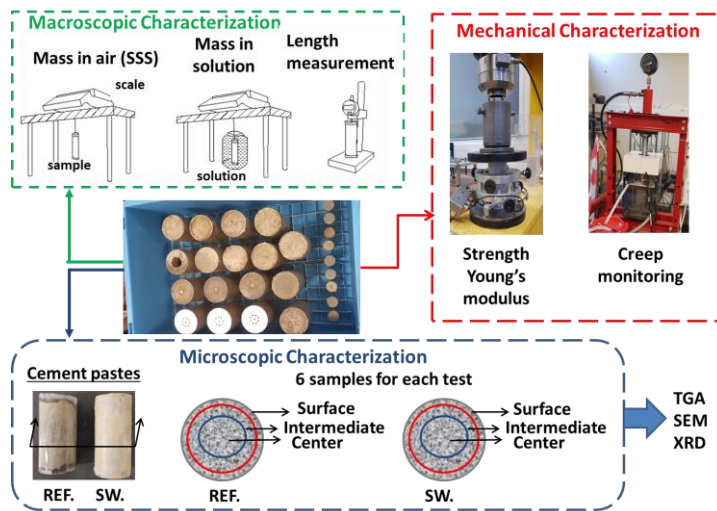


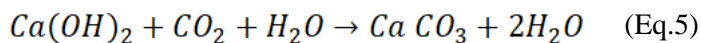
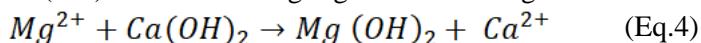
Table 1 : OPC composition and properties

C ₃ S	60.00%
C ₂ S	16.30%
C ₃ A	7.70%
C ₄ AF	10.50%
Gypsum	3.50%
Other constituents	2%
Density (10 ³ kg/m ³)	3.16
Blaine (m ² /kg)	400

Fig. 2 : Multi-scales experimental chemo-mechanical characterization

3. Results and discussions

Fig.3 shows the evolution of product thickness deposited at the mortars surface and Fig.6 shows the evolutions of phases formed at the paste surface sample. It can be seen that the samples recorded a positive thickness indicating that new products have been formed at the surface. The thickness deposited at the surface of hollow cylinders was higher than that of plain cylinders. This can be explained by the higher exposure surface of hollow cylinders. Thickness evolutions are linear with respect to the square root of time, highlighting the ions diffusions following Fick's law. This could show the diffusion of ions on the surface and their reaction with the cement phases to form this deposited layer. The phases formed at the sample's surface was identified using TGA (Fig.4). Results show the formation of brucite Mg(OH)₂ and calcium carbonate CaCO₃ and the consumption of Ca(OH)₂. The results highlight the following reactions:



Calcium carbonate was also found on the surface of control samples (Ref.). In these samples, calcium carbonate formed rapidly during the first 30 days and then gradually decreased or stabilized. Previous groundwater studies have shown that calcium carbonate can form.

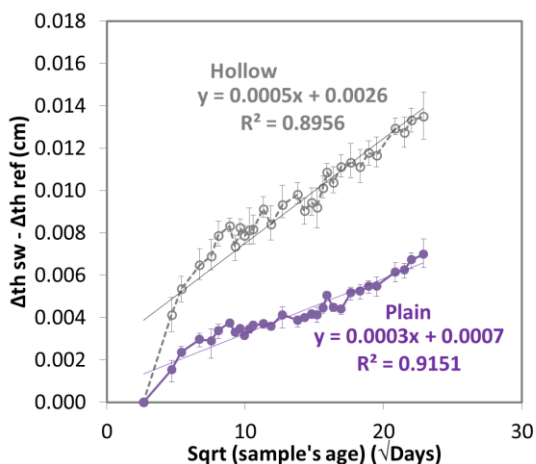


Fig. 3 : Evolution of material thickness deposited at the sample surface

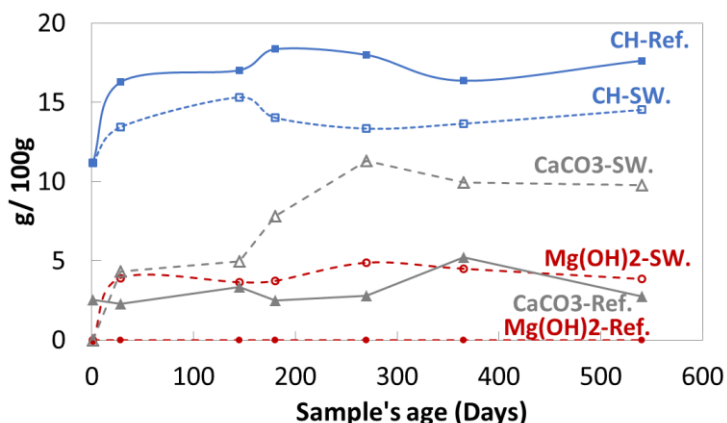
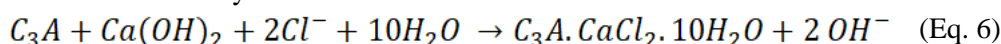


Fig. 4 : Phases identification at the sample's surface using TGA analysis

Fig.5 summarizes the phases identified using XRD analysis at the surface and the center of control and SW samples after one year of exposure. Fig. 6 shows the chloride profiles for control and SW samples identified using energy dispersive spectroscopy analysis.

It can be seen that brucite, located at $2\theta=37.966^\circ$, is only observed on the surface of samples immersed in seawater. This is in agreement with the results obtained using TGA analysis (Fig.4). Similarly, Friedel's salt was identified in the SW samples at peak $2\theta=11.193^\circ$ confirming the reaction of chloride ions with cement hydrates.



Unlike brucite, Friedel's salt could be detected in the center and on the surface of the samples immersed in the marine solutions, which could confirm the diffusion of chloride ions from the surface to the center of the samples. This diffusion was detected in Fig.6 using EDS analysis. The expected gypsum peak at ($2\theta=11.438^\circ$ and $2\theta=20.731^\circ$) could only be observed at the surface of samples immersed in a marine solution at an advanced age of immersion (one year). Aragonite and vaterite formed on the surface of the exposed samples, confirming the greater amount of $CaCO_3$ observed in the TGA analysis on the surface of samples exposed to seawater (Fig.4). Calcite was observed in both control and exposed samples. The ettringite peak appeared in both cases of immersion. This does not indicate that its formation is favored in seawater. Sulfate attack generally induces expansion by crystallization pressures due to ettringite formation. The longitudinal expansion remained very small during the experiments [7]. Thus, sulfate attack had less influence due to the chloride penetration [5] and the formation of Friedel's salt.

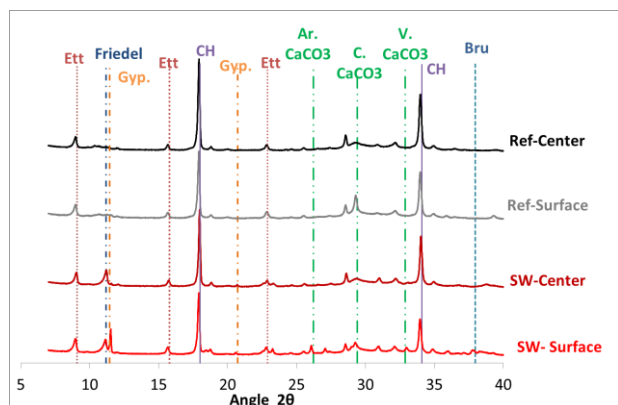


Fig. 5: XRD phases identification after one year exposure for control and exposed pastes

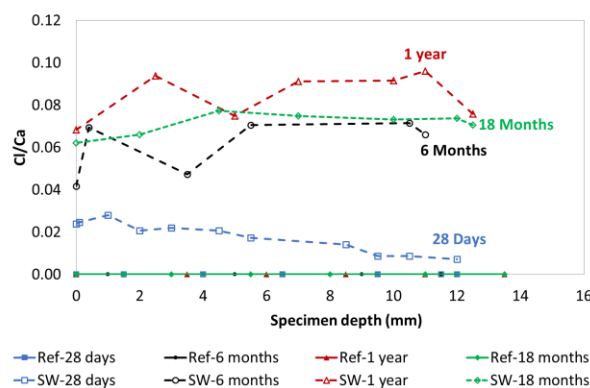


Fig. 6: Chloride profiles identified using energy dispersive spectroscopy analysis

According to the chemical reactions observed in the last figures, the microstructures have been numerically built in CEMPP with the same volume fractions of components. Fig.7 shows the maximum creep compliance (J_{\max}) recorded after 3 years of loading as a function of the proportion of C-S-H present in the cement pastes microstructure. This graph joins the simulations performed at the following loading ages: 7 days, 14 days, 28 days, 2 months, 4 months, and 6 months (one point per layer and per loading age). Fig. 8 shows a great agreement of the comparison between the numerically calculated specific displacements due to creep applied at age 28 days and those experimentally monitored for control and attacked hollow mortars. Fig.7 allows concluding that the ettringite-rich layer (layer V) recorded the highest creep and the gypsum-rich layer (layer IV) recorded the lowest creep, regardless of the age of load application. It should be noted that the expansive character of ettringite (crystallization pressures) is not taken into account by the model, as the experimental results obtained did not show any macroscopic expansion and damage after two years of follow-up [7]. The attacked multilayer microstructure (SW) recorded a creep lower than the control sample. This can be explained by the lower amount of C-S-H present in the microstructure especially due to the presence of layer III simulating the C-S-H consumption. The adopted model restores the difference between the chemically modified layers even with the same rate of C-S-H in these microstructures. Globally, this is consistent with the mechanical model hypothesis which considers that C-S-H in the main phase involved in creep.

In Fig.8 it can be observed that the creep displacements for reference mortars are slightly higher than for attacked mortar and that the effect of seawater attack-creep coupling is not predominant at long term. This compensation between positive and negative effects can be explained with the difference in the behavior of layers (Fig.7). To explain these findings, complimentary experiments have to be carried out and analyzed.

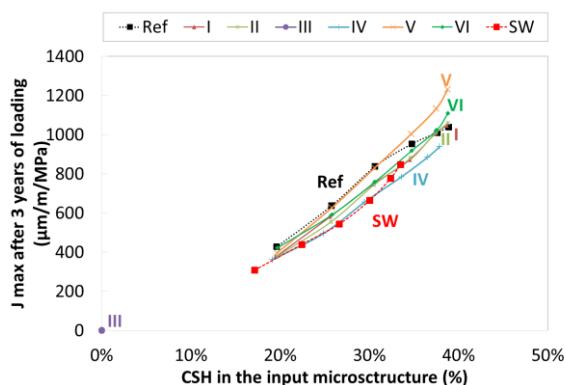


Fig. 7 : Creep compliance and CSH content of chemically modified layers of cement paste

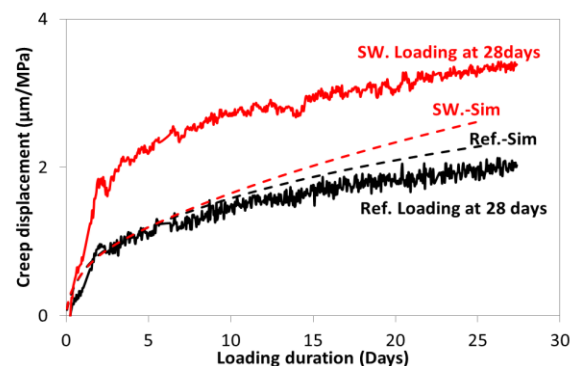


Fig. 8 : Creep displacement of mortars: Experimental vs. numerical approach

4. Conclusions

A numerical multiscale model has been developed to analyze the mechanical creep behavior of cementitious materials in seawater. A new experimental test has been performed for the same goal. The mechanical creep behavior of attacked samples remained equal to that of the reference samples, even though significant microstructural changes and rapid penetration of chloride ions were observed at the microscopic level. Experimental analysis added explanation on the type of products formed during attacks. Mortar and cement paste cylinders were characterized by the highest amount of

products formed as a result of exposure to seawater. The material deposited at the surface of specimens was identified by microscopic characterization methods (SEM/EDS, XRD, and TGA). The protective effect of brucite and calcium carbonate surface layers could be detected. Their linear evolution as a function of the square root of time follows Fick's law. Sulfate attack in seawater was not predominant, with minor expansion and ettringite formation, and the pore blocking effect of brucite and calcium carbonate near the surface could have slowed down ionic diffusion in the cement matrix. Similarly, this could be attributed to the presence of chloride ions that mitigate sulfate attack. By considering these chemical effects in the model, simulations of creep for cement pastes and mortars have been performed. After validating the model, it has been used to explain the creep evolution due to a competition between the dissolution-formation of the cement paste's components and the loading. This model will now be used for the simulation of concrete structures by considering the interaction between the last effects and the physical properties of aggregates and reinforcement.

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