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Studying concrete blocks in real environments and comparing to laboratory experiments

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Abstract. The main cause of premature deterioration of reinforced concrete structures is the corrosion of steel bars, induced by chloride ions (for example in marine environment) or by carbonation. At the same time, environmental-induced degradations of concrete can also affect the structure, such as external sulphate attack leading to the formation of ettringite, inducing expansion inside the materials and finally degradation.

In this paper, concrete blocks (with supplementary cementitious materials), exposed to real environments, are studied and compared to laboratory experiments. Various aspects of the microstructure and of the pore structure are investigated, by using Mercury Intrusion Porosimetry and XRD, TGA, ²⁷Al NMR, in order to better understand the results obtained relatively to the apparent chloride diffusion coefficients and to the chloride binding for example in marine environment.

Results show the difference between the microstructures of the various materials and their consequences on the ingress of aggressive agents.

Keywords: Durability, In situ, SCM

1 Introduction and experimental

Corrosion of steels bar is one of the main causes of reinforced concrete degradation [1-2]. This corrosion can be induced by chloride ingress in marine environments or in the presence of deicing salts. In addition, local environment can contain sulphate which may react with the cementitious matrix leading to the formation of ettringite. Thus, this can induce expansion and finally degradation inside the materials [3]. Numerous studies describe these two phenomena separately but a few studies state a possible coupling [4-5] which is the aim of the present work.

There are few parameters which influence these ingress and in particular, the porous network. In addition, Chloride ingress is delayed by interactions between chlorides and

the cementitious matrix [7-9] and the same for sulphate ingress. Consequently, both sulphate and chloride react with the same cementitious phases (C-S-H or aluminates phases) and a competition between these two ions can occur in marine environment [4-6].

The aim of this research is first to investigate the porous network of cement pastes (OPC alone or with SCMs such as métakaolin (MK), fly ash (FA) or slag (GGBS)) in order to then, understand the chloride ingress in presence of sulphate in NaCl contact solutions. In particular, chloride diffusion tests were performed in presence or not of sulphate in contact solution. The microstructure is investigated here by Mercury Intrusion Porosimetry (MIP), thermogravimetry (TGA-DTG), and ^{27}Al NMR spectroscopy. In addition, an experimental campaign has been carried out on a concrete with fly ash (concretes with another SCMs are not figured here), which is exposed during 20 years at marine conditions.

2 Results and discussion

The experimental results demonstrated that the porous network is different as SCM is used in the mixture (see Fig. 1). At long term, using SCM in cement paste upgrades the porous network (Average diameter decreases and tortuosity probably increases) despite the increases of the global porosity for some materials. In addition, the water curing time is fundamental for the development of the porous network in order to obtain the best performance of the materials, in particular for concrete with SCM.

Consequently, Chloride ingress is less marked in cement pastes with SCM (see Fig. 2). However, the results presented here are obtained on materials after 365 days of water curing. Since the porous network continues to evolve until 365 days for cement pastes with SCM, $D_{\text{app,Cl}}$ evolve too depending of the state of hydration and, in real environment, of the drying conditions. In addition, some cementitious matrices with SCM can bind more chloride (MK cement pastes) than CEM I which also decreases the $D_{\text{app,Cl}}$.

In addition, chloride ingress is accelerated by the presence of sulphate in contact solution. This increase is explained by a change in the microstructure and the pore solution but also by a lower chloride binding. With regard to chloride ingress, there are differences between the various cementitious matrices. Cementitious matrixes with high metakolin or slag content are more resistant to the effect of the presence of sulphate in the contact solution (probably due to a higher binding capacity).

Comparison of these results with a concrete in real sea conditions (see Fig. 3) is difficult since the presence of other parameters (pH, temperature, contact solution with other ions (Mg^{2+} , ...), drying effect..). However, it is quite promising because the different technics used (XRD, TGA and ^{27}Al NMR) in order to establish a profile, show almost the same results. For example, close to the surface (0-11mm), there is of course ettringite but also the presence of Friedel's salt, however the ratio free Chloride

on bound chloride is the highest measured of all depth and moreover, SO_3 concentration is the highest. This means a competition between chloride and sulphate to bind to cementitious matrix and consequently cementitious matrix bind less chloride in presence of sulphate. Deeper inside the concrete (13-23mm), ettringite amount is considerably reduced (as well as SO_3 concentration) and amount of Friedel's salt seem to be higher confirmed by elementary analysis showing the highest amount of bound chloride. At 34-44mm, ettringite amount is equal to its surface amount and it seems there is solid solution between Friedel's salt and hemicarboaluminate. At 55-60mm, there is still traces of Friedel's salt, which is in accordance with chloride front measured at 93mm, but the main AFm phases are hemicarboaluminate and monocarboaluminate (phases here without external attack).

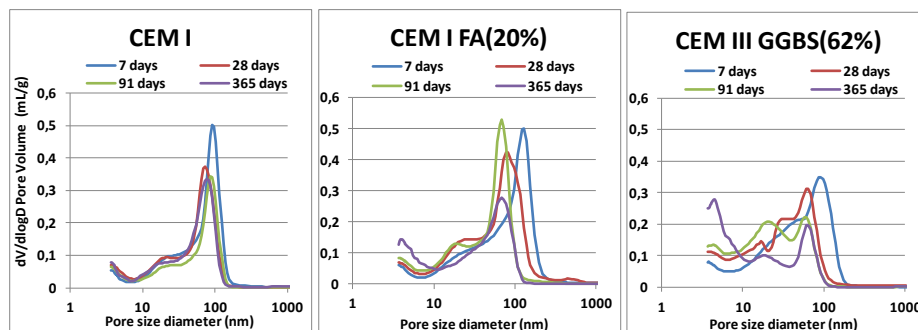


Fig. 1. Pore size distribution as a function of water curing time obtained by MIP for few cement pastes.

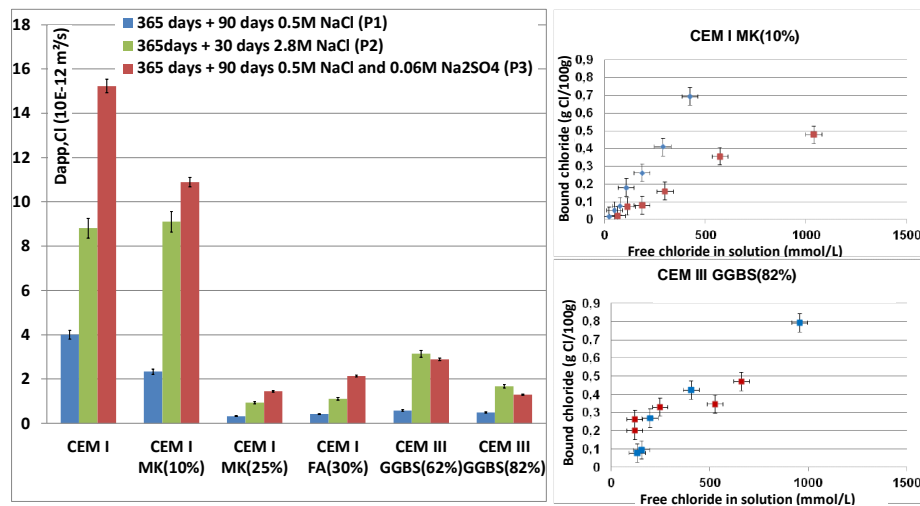


Fig. 2. Chloride apparent coefficients ($D_{app,Cl}$) (in left) and CBIs obtained by profile method (in right) on cement pastes after 365 days of water curing and contact with solutions.

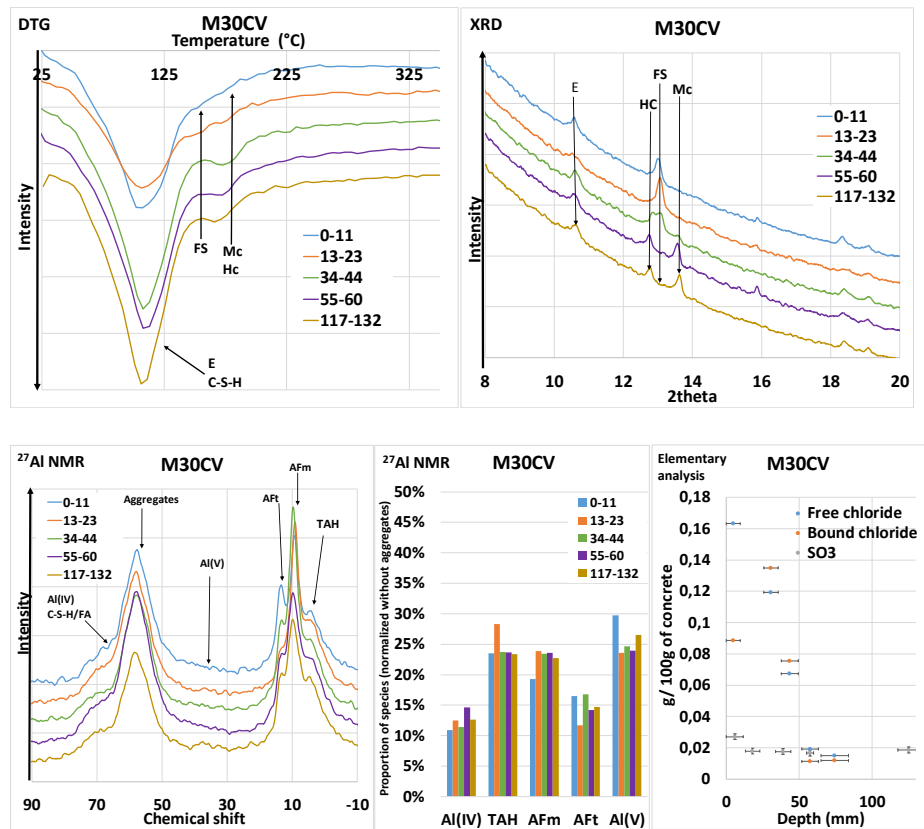


Fig. 3. DTG, XRD, ^{27}Al NMR and elementary profiles (mm) of a concrete exposed to sea during 20 years. E: ettringite, FS: Friedel's salt, Mc: monocarboaluminate and Hc: hemicarboaluminate. Chloride front (measured by AgNO_3) is equal to 93mm.

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