



Chloride binding in sound and carbonated cementitious materials with various types of binder



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HIGHLIGHTS

- Chloride ingress has been investigated on sound and carbonated materials.
- We study the effect of supplementary cementitious materials on concrete durability.
- We quantify the changes of cementitious matrix and a decrease of chloride binding.
- Decalcification of hydrated phases is responsible for a decrease of Friedel's salt.
- In carbonated materials, C–S–H lose their chloride binding capacity.

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ABSTRACT

Carbonation and chloride ingress are the main causes of reinforced concrete structures degradation. Usually, these two phenomena are studied individually. Here, chloride ingress has been investigated on sound and carbonated cementitious materials (cement pastes and concrete). The supplementary cementitious materials (SCM) are fly ash, slag and métakaolin. The materials were carbonated by exposure to accelerated conditions (1.5% CO₂ and 65% RH) in laboratory. Chloride binding isotherms of sound and carbonated samples were assessed by the equilibrium method (exposure to various alkaline NaCl solutions). The microstructure was characterized not only by usual techniques such as XRD and TGA–DTA, but also by ²⁹Si and ²⁷Al NMR spectroscopy. The results show that carbonated samples bind less chlorides than sound ones. The use of a combination of various techniques of microstructural characterization reduces the number of the possible explanations of these findings. In carbonated materials, both the quantity of Friedel's salts and of chlorides bound by C–S–H decrease. The first decrease can be explained by a lack of portlandite and modification of aluminate phases equilibrium. The second decrease seems to be due to a modification of the C–S–H (change of surface charge) during the carbonation process. Moreover, differences according to the nature and the amount of supplementary cementitious materials (SCM) were observed.

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1. Introduction

Corrosion of reinforcement is one of the main causes of reinforced concrete degradation. This corrosion is due to carbonation or chloride ingress. If the corrosion of reinforcement due to chloride ions occurs more often in marine environments or in the presence of deicing salts, carbonation occurs systematically, in a more or less high degree, depending of the environmental conditions

(relative humidity, temperature, etc.). Numerous studies describe these two phenomena separately [1–5] but a few studies state a possible coupling [6,7].

In CO₂-free environment, the hydrated Portland cement consists of hydrated phases in equilibrium with a pore solution whose pH is around 13.5. In marine environments or in the presence of deicing salts, chloride ions can progress through this pore solution up to steel rebars. This progress is delayed by interactions between chlorides and the cementitious matrix [8–12]. Chemical interactions lead to the formation of Friedel's salt (FS) [9–11,13]. Furthermore, a given amount of chlorides, which depends in particular on the pH of the pore solution, binds onto the C–S–H (physical binding) [11,12,14–17]. These binding mechanisms are changed by

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carbonation. Under natural conditions of temperature and pressure, the atmospheric CO_2 is dissolved into the pore solution to form H_2CO_3 which, by dissociation, decreases the pH of the pore solution [6,18–20]. Portlandite ($\text{Ca}(\text{OH})_2$) plays the role of buffer and maintains the pH of the pore solution at $\text{pH} = 12.5$ by releasing adequately OH^- ions. During the carbonation process, the dissolution can affect not only $\text{Ca}(\text{OH})_2$ but also C–S–H, AFm, Aft, etc. [5,6,18,20]. The changes in chloride binding induced by carbonation are particularly significant when the mixture contains supplementary cementitious materials (SCM) [9,20–22]. Binders which contain ground granulated blast furnace slag (GGBS) for example are used in marine environment since the chloride diffusion coefficient of GGBS-mixtures is significantly reduced. But these binders form less portlandite than OPC binders [20,23,24]. Consequently, for a same exposure environment and time, carbonation ingress in these materials is higher than in OPC binders [20] as also expected for binder with fly ash and metakaolin.

The aim of this research is to investigate the effect of the binder type on chloride binding and to better understand the coupling between carbonation and ingress of chloride ions. An experimental campaign has been carried out on various cementitious materials with or without SCM. SCMs are here GGBS, fly ash (FA) or metakaolin (MK). In particular, chloride diffusion on both sound (i.e. non-carbonated) and carbonated cementitious materials is studied. Microstructure is investigated by differential thermogravimetry (TGA–DTG), X-ray diffraction (XRD) and ^{29}Si and ^{27}Al NMR spectroscopy. Quantification of the various mineral phases has been obtained by combination of these techniques.

2. Experimental

2.1. Materials studied

Various concretes were designed with the same clinker and granular skeleton using siliceous aggregates. The main constituents of the clinker are given in Table 1 and Table 2. The binder content is 300 kg/m^3 and the water to binder ratio (w/binder) is equal to 0.53 for all the mixtures. Studied binders are CEM I (OPC with 97% clinker), CEM III/A (with 62% GGBS) denoted CEM III GGBS(62%), CEM III/C (with 82% GGBS) denoted CEM III GGBS(82%), CEM I + 30% FA denoted CEM I V(30%), CEM I + 10% MK denoted CEM I MK(10%) and CEM I + 25% MK denoted CEM I MK(25%). Cement pastes with the same binders were also prepared with w/binder = 0.50.

Two water-curing times are chosen (90 days and 1 year) in order to take into account the evolution of the microstructure as a function of the age. Sound samples (i.e. non-carbonated) will be denoted “reference” in the paper.

2.2. Crushed samples and carbonation process

Accelerated carbonation tests are often used to carbonate samples in laboratory as an alternative technique to the natural carbonation process which is much longer [3,5]. Tests consist in, after drying, leaving samples in an environment enriched in CO_2 at an optimal relative humidity (40–65%) [3]. Different rates of CO_2 are applied in the literature in accelerated tests. According to [5], a too high rate can modify the microstructure more than a natural carbonation rate would. A drying process increases carbonation ingress but a too high temperature affects cementitious phases such as ettringite. In this study samples were carbonated in accelerated conditions (by two different procedures) before contact with NaCl solutions. The following carbonation protocols (see Fig. 1) have been chosen: after water curing, slices of concretes or pastes are dried during 3 days at 60°C . Then the slices are crushed. The size of the crushed pieces is lower than 2.5 mm. A part of the crushed samples is preserved in CO_2 -free environment (reference samples). The other part

Table 2

Mineralogical composition of the CEM I from BOGUE calculation (%).

	C_3S	C_2S	C_3A	C_4AF
CEM I	51.23	28.32	9.90	8.81

of crushed samples is carbonated in chamber (1.5% CO_2 and 65% RH) during 3 days or exposed to carbonation until constant mass (around 2 months). These two times of carbonation are used to show the effect of a partial carbonation (PC) or a total carbonation (TC) in comparison of the reference state (Ref).

2.3. Chloride binding isotherms obtained by the equilibrium method

Chloride binding isotherms (CBIs) have been obtained here by the equilibrium method. The equilibrium method [12,25] consists in putting crushed specimens (see Section 2.2) of pastes or concretes (Ref, TC and PC, see Fig. 1) in contact with NaCl solutions during two months. Six contact solutions (0, 0.05, 0.25, 0.5, 1 and 1.5 M NaCl + 0.1 M NaOH) are tested. Equilibrium binding is reached at the end of the test. The remaining amount of chlorides in the solutions (F) (equal to the quantity of free chlorides in pore solution at the end of the experiment) is measured as well as in solutions without samples (T) after two months of contact. The difference between T and F is equal to the chloride bound quantity (B). CBIs represent the equilibrium between chlorides bound (B) to the cementitious matrix and free chlorides (F) in the pore solution, $B = f(F)$ [12]. The originality of the present study is to assess CBIs for both (PC) and (TC) samples and for both cement paste and concrete samples.

2.4. Microstructural characterization

2.4.1. TGA–DTG

Thermogravimetric analyses (TGA) and differential thermogravimetry analyses (DTG) [3] were performed with a simultaneous thermal analyzer by heating from 25°C to 1150°C with $25^\circ\text{C}/\text{min}$ steps. These techniques are used here to quantify the water lost from calcium hydroxide (portlandite) and C–S–H + Ettringite (noted C–S–H + E) as well as the CO_2 lost from calcium carbonates of the samples as illustrated in Fig. 2. They were applied to 90-day water-cured crushed Ref and PC samples of pastes. They were also applied to 1-year water-cured crushed Ref and TC samples of pastes (see Fig. 1).

2.4.2. XRD

X-ray diffraction [7] allows one to identify the crystallized phases (e.g. portlandite, calcium carbonates, monocarboaluminate, etc.) and to estimate their proportions. Such analyses have been carried out here on crushed pastes, carbonated in chamber (1.5% CO_2 and 65% RH) or not (PC, TC and Ref samples) and after contact with NaCl solutions during 2 months (see Fig. 1). In this work, relative intensities of Friedel’s salt peak area (reflecting the quantity of FS in samples) will be observed and compared to the CBIs. The aim is to distinguish the two types of bound chlorides (the chemically and the physically ones).

2.4.3. NMR

NMR spectroscopy [26] gives access, at a local scale, to the immediate environment of a nucleus. ^{27}Al and ^{29}Si nuclei have been here observed by the MAS (Magical Angle Spinning) technique [26–29]. Geometrical configurations of a nucleus are a function of the chemical shift (see Figs. 3 and 4). NMR spectra have been obtained on a Bruker Avance 500 MHz apparatus (11.74 T magnetic field).

Geometrical configurations of aluminum can be observed by ^{27}Al NMR [27,28] (see Fig. 3). Aluminum in tetrahedral configuration Al(IV) is generally attributed to aluminum substituted for silicon in C–S–H chains and residual anhydrous cement. Aluminum in octahedral Al(VI) configuration is divided into three components: Aft, AFm and a constituent which is, according to Andersen et al. [29,30], an amorphous/disordered aluminum hydroxide or a calcium aluminate hydrate (TAH) not observed by XRD [29]. Finally, aluminum in pentahedral configuration Al(V) represents aluminum substituted for calcium in the C–S–H interlayers or present in

Table 1

Chemical composition of the cement and SCM tested (%).

	CaO	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	MgO	Na_2O	K_2O	MnO	SO_3
CEM I	62.53	19.54	2.90	4.98	0.30	0.84	0.30	0.82	0.09	2.97
CEM III/A	49.77	29.86	1.28	8.10	0.46	4.61	0.40	0.56	0.16	2.29
CEM III/C	45.70	32.00	1.00	9.90	0.50	5.80	0.63	0.54	0.20	2.00
MK	0.00	66.29	4.29	21.30	1.12	0.25	0.84	0.49	0.00	0.08
FA	0.00	51.59	6.58	23.78	1.03	0.49	1.09	3.05	0.11	3.05

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