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Marine Biofilm effect on mortar surface layer.

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Abstract. The objective of this study is to evaluate the effect of biofilm development on the surface layer of a mortar. This work aims at understanding the modifications occurred within the cementitious matrix such as its composition as its microstructure following the bio-colonization. These properties were studied after 360 days of immersion in two immersion media (Artificial Seawater (AS) and Natural Seawater (NS)) using ATG/DTG, XRD analyses and SEM observations. It was found that the biofilm caused the dissolution of the portlandite deeper than when the mortar was not colonized (AS medium). Moreover, a strong carbonation was observed in the first millimeters of the matrix. Two polymorphs of calcium carbonate were particularly identified. Aragonite is the dominant form present on the surface of the mortar immersed in NS. Calcite and magnesian calcite were also observed but after bio-colonization of the mortar. Thus, the development and the biological activity of the biofilm seems to modify the properties of the mortar and could control the precipitation of calcium carbonates on its surface.

1. Introduction

Cementitious materials are bio-receptive in the marine environment [1,2]. Indeed, these substrates are immediately covered by a thin layer of biofilm, which constitutes the first phase of bio-colonization. The biofilm is composed of a succession of benthic communities (mainly diatoms [3]) that promote the second phase of colonization with the attachment of macro-algae and other sessile organisms [3,4].

The objective of this study is to study the interaction between a cementitious material and a marine biofilm. The substrate used is a mortar. When the latter is immersed in the marine environment, it is subjected to different types of physical, chemical [7-10] and biological [11] attacks that can have an impact on its matrix. Indeed, the development of a biofilm on the surface of the mortar can lead to its bio-deterioration. Hueck, (1965) [12] defined biodeterioration as "*any undesirable change in the properties of a material caused by the vital activities of organisms*". Several studies [13-15] have shown that some ions of the cementitious matrix released into the water column can be assimilated by microphytobenthos and macroalgae for their metabolism.

Mesocosm and laboratory studies were conducted to investigate the evolution of the microstructure and composition of the surface layer of the mortar once biocolonized after 360 days of immersion. The following techniques were used jointly for this work: Thermogravimetric analysis (TGA/TDG), Scanning Electron Microscope (SEM) observation and X-ray Diffraction (XRD).

2. Materials and Methods

2.1. Experimental Setup

For this study, mortar samples were made from CEM II/A-LL cement and siliceous alluvial sand (Ø 0/2 mm). The samples studied (Ø110mm/H50mm and Ø110mm/H110mm) were prepared according to the NF EN 196-1 standard and then exposed to a Relative Humidity (RH) of 100% for 24 hours, before being demoulded and stored in water for 90 days at room temperature. After 90 days of curing at 100% RH, the samples were immersed in natural seawater (NS) (mesocosm at the CREC station in Luc-sur-Mer, FR). To distinguish the effect of chemical attack of the seawater from the effect of bio-colonisation on the mortar, samples were also immersed in the laboratory in artificial seawater (AS) obtained from the dissolution of Instant Ocean© salt, Spectrum Brand dosed at 33.3 g.L^{-1} [16].

2.2. Evolution of the microstructure and composition of the mortar surface layer

2.2.1. Thermogravimetric analysis (TGA/TDG). Thermogravimetric analyses provide information on the evolution of the mineralogical composition of the material. These analyses were carried out using an STA 449 F5 (Netzch). Tests were carried out over a temperature range of 20°C to 1000°C, with a heating rate of 10°C/min and a nitrogen atmosphere of 50 mL/min. The tests were carried out on powder samples obtained after sampling the surface layer (0 to 10 mm deep every two millimetres) of the reference mortar (after 90 days of curing) and on samples after their immersion (AS and NS medium).
From the thermogravimetric analyses, it is possible to estimate the amount of portlandite and calcium carbonates present in the mortar.
The amount of initial portlandite is determined from the measurement of the amount of water released by mass loss according to the equation (1) :

$$m_{portlandite} = \frac{M_{portlandite} \times m_{water}}{M_{water}} \tag{1}$$

With $m_{portlandite}$ the mass of portlandite (g), $M_{portlandite}$ the molar mass of portlandite (73 g.mol^{-1}), m_{water} the mass of water (g) lost during the temperature rise (between 400 and 600°C) specific to the decomposition of the portlandite and M_{water} the molar mass of the water (18 g.mol^{-1}).
As with portlandite, it is possible to estimate the amount of calcium carbonate present in the material using the loss of mass from carbon dioxide according to the equation (2) :

$$m_{CaCO_3} = \frac{M_{CaCO_3} \times m_{CO_2}}{M_{CO_2}} \tag{2}$$

With m_{CaCO_3} mass of $CaCO_3$ (g), M_{CaCO_3} the molar mass of $CaCO_3$ (100 g.mol^{-1}), m_{CO_2} the mass of carbon dioxide (g) lost during the temperature rise specific to the decomposition of the $CaCO_3$ (between 600°C and 1000°C) and M_{CO_2} the molar mass of CO_2 (44 g.mol^{-1}).

2.2.2. Scanning electron microscopy (SEM). The morphology of the main mineral components of the mortar, at the micrometric scale, was analysed using a JEOL 7200 LV Scanning Electron Microscope (SEM), an instrument of the CRISMAT laboratory (Caen, France). The samples (Ø110mm/H110mm) were fixed with 2.5% glutaraldehyde for a few days in 0.2M sodium cacodylate buffer pH 7.4 in the presence of 7% sucrose, then rinsed in this buffer. The samples were then dehydrated by progressive alcohol baths and dried under vacuum (200mbar) after two HMDS (hexamethyldisilazane) baths. The samples are glued on a SEM pad with a carbon glue tape to evacuate the charges.

2.2.3. X-ray diffraction (XRD). The surface of the samples (Ø110mm/H110mm) was characterised using the TFS 4-circle diffractometer (Ecocorail) equipped with a CPS 120 detector and a Cu K wavelength of Cu $K\alpha_{12}$ [17]. The diffractometer is calibrated on a NIST LaB6 standard powder (srm 660a). The latter was used to calibrate the instrumental contribution [18]. An angle of incidence w=3° and an acquisition time of 12 hours were used. The footprint of the beam size on the sample surface remains within the 1-2 mm^2 during the measurement.

The identification and quantification of the phase was done by referring to the Crystallography Open Database (COD) [19] and by performing a Rietveld refinement operated using MAUD [20].

3. Results and Discussions

3.1. Mortar composition from thermogravimetric analysis (ATG/DTG)

Initially, the mass percentage of portlandite in the surface layer (from 0 to 10 mm) of the mortar studied has an average value of 6.3% (Figure 1a). After immersion, the amount of portlandite decreases only in the first two millimetres in the mortar immersed in the AS medium, whereas it continues to dissolve deeper in the mortar immersed in the NS medium reaching 4.4% between 6 and 8 mm depth. As a result, the microphytobenthos accelerates the dissolution of the portlandite in the cement matrix

As for the mass percentage of calcium carbonates in the mortar, the average value is 2.3%. Once the mortar is immersed in the two media studied, the quantity of calcium carbonate increases only in the first two millimetres of depth (Figure 2b). The increase in $CaCO_3$ may be due to the carbonation of the portlandite following its dissolution (Figure 2a). This carbonation is greater at the surface of the mortar immersed in the AS medium (12.2%) than when it is colonised (6.8%). This difference can be explained on the one hand by the decrease in the quantity of Ca^{2+} ions in the medium following its assimilation by the microphytobenthos. On the other hand, the fixation of dissolved CO2 during photosynthesis reduces its availability in the water column. The form of the neoformed $CaCO_3$ will be more precisely identified after the analysis of the samples by XRD.

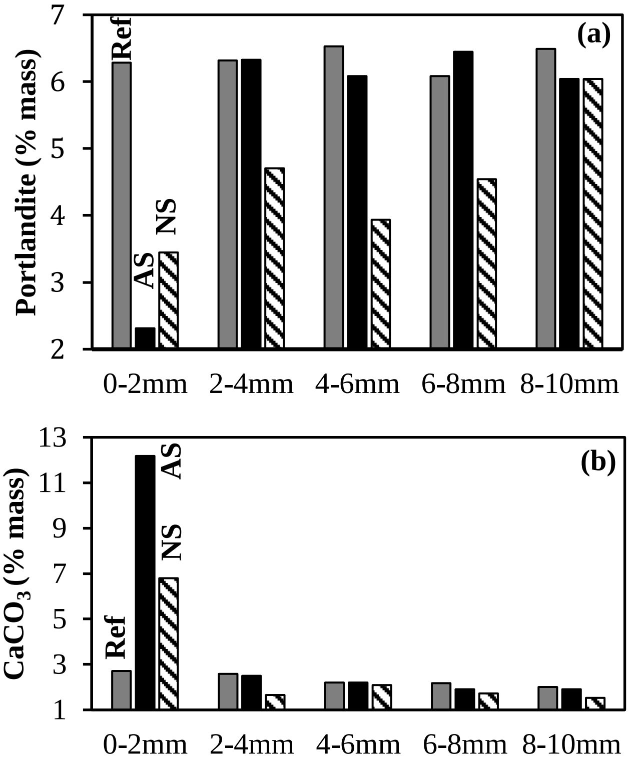

Figure 1. Mass percentage (%) of the amount of portlandite (a) and the amount of calcium carbonates (b) as a function of depth (0 to 10 mm) in the reference mortar (Ref) and the mortar immersed after 360 days in artificial seawater (AS) and in natural seawater (NS).

3.2. Scanning Electron Microscopy (SEM)

Figure 2a show the appearance and texture of the material studied before its immersion. The facies of the different phases initially found in the cement paste are difficult to distinguish. However, we can clearly observe C-S-H gel. Once immersed in the AS medium, the mortar shows orthorhombic crystals on its surface, characteristic of aragonite (Figure 2b) [21]. he precipitation of aragonite is due to the strong presence of magnesium ions in the sea water [22]. Changes in the morphology of the neo-formed carbonates are observed on the surface of the mortar immersed in natural seawater (NS). Indeed, aragonite was found but in the form of cauliflower and another phase which can be similar to calcite (Figure 2c et d). Further XRD analysis will allow the specification of the calcium carbonate polymorph identified.

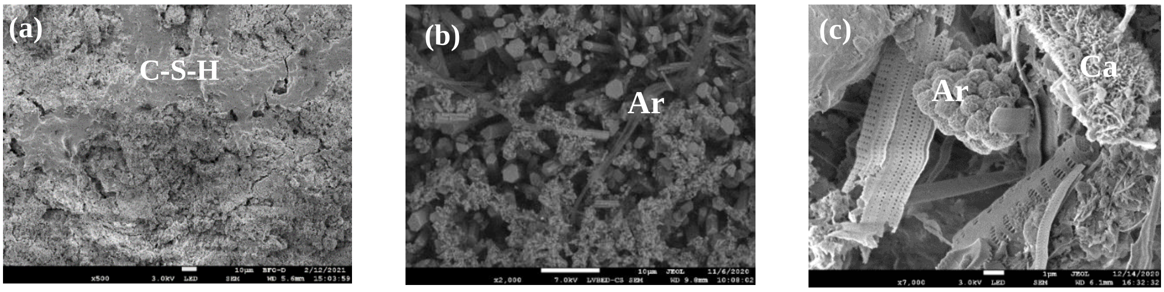

Figure 2. SEM observations of a mortar: reference (before immersion) (a); immersed after 360 days in Artificial Seawater medium (b); in Natural Seawater medium (c) (C-S-H : gel de Calcium-Silicate-Hydrate ; Ar : Aragonite ; Ca : Calcite).

3.3. Scanning Electron Microscopy (SEM)

Mineralogical analysis by X-ray diffraction (XRD) was carried out in order to compare the nature of the crystallised mineral phases present on the surface of the non-immersed mortar (reference) and immersed in the two media studied (AS, NS). The mineralogical composition of the surface of the reference sample consists of quartz and calcite (Tableau 1). Calcite represents 95.7% of the sample. This result means that the reference sample was carbonated before its immersion in the different media studied. This carbonation has a positive effect on the kinetics of bio-colonisation since some studies [23,24] have shown that it improves the initiation of biofilm on the surface of the cementitious material.

In AS, a decrease of calcite in favour of aragonite is observed (confirmed by SEM observations (Figure 2b)). Abiotic factors (high concentration of Mg^{2+} ion) of the environment can explain the preponderance of aragonite.

In the NS environment, three forms of calcium carbonates were observed. The presence of magnesian calcite is explained by the incorporation of Mg^{2+} ions in the crystal structure of calcite [25]. These results show that the development of biofilm on the mortar surface may have caused a change in the crystal lattice structure of the calcite.

Table 1. Percentage (%) of crystallised mineral phases on the surface of a reference mortar and after 360 days of immersion in Artificial Seawater (AS) and Natural Seawater (NS).

	Reference	**EA**	**EN**
Halite	-	15.3 (+- 0.5)	-
Aragonite	-	62.8	38.6 (+- 2.7)
Calcite	95.7	21.8 (+- 1.9)	30.5 (+- 2.2)
Calcite Mg	-	-	28.3 (+- 2.1)
Quartz	4.23 (+- 0.1)	-	2.5

4. Conclusions

The different techniques applied in this study provide complementary results necessary to understand the interactions taking place within the mortar surface layer once the material is colonised.

The development and biological activity of the biofilm caused an acceleration of the leaching of portlandite within the cement matrix. Calcium ions released into the medium can then be assimilated by the microphytobenthos.

Aragonite is the majority form on the surface of mortar immersed in artificial seawater. In natural seawater, other forms of calcium carbonates were observed such as calcite and magnesian calcite. The biofilm was able to control the precipitation of calcium carbonate on the mortar surface.

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