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## **CORROSION PROCESSES AND ECE TREATMENT IN A BOTH CARBONATED AND CHLORINATED REINFORCED CONCRETE**

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### **Abstract**

Civil engineering structures and historical buildings can suffer from corrosion of the embedded reinforcing steel once the concrete cover is totally carbonated and/or when chloride ions reached the steel/concrete interface. On field, these two types of contamination can be encountered separately or combined requiring implementation of proper repair methods.

In this study, both chlorinated and carbonated reinforced concrete specimens were followed by three main analysis means: Raman microspectroscopy, electrochemical characterization and scanning electron microscopy. They were first characterized during the two-step aging process, chlorides addition and complete cover carbonation. Electrochemical chloride extraction was then performed as a repair treatment (1 A/m<sup>2</sup> of steel surface during 8 weeks). Its efficiency and its impact on the specimen interface and cement matrix were studied.

Study of rebar's electrochemical characteristics during the aging notably showed an increase of corrosion rate from negligible value of 0.1  $\mu\text{A}/\text{cm}^2$  after fabrication to above 10  $\mu\text{A}/\text{cm}^2$  after carbonation. SEM observations confirmed this phenomenon with the identification of a corrosion layer on most of the concrete/steel interface after carbonation. The ECE efficiency was put in evidence by a decrease of Cl<sup>-</sup> concentration below the theoretical threshold value of 0.4 % mass of cement after two weeks. Simultaneously a realcalinisation was observed around the reinforcement bar which reached about 1 cm in 28 days.

**Keywords:** chloride, carbonation, corrosion, chloride extraction, Raman microspectroscopy, scanning electron microscopy, electrochemical characterization

## 1. Introduction

Complete cover carbonation and chloride ions penetration until the steel/concrete interface are the two main causes of reinforced concrete degradation induced by corrosion. These two types of contamination can be encountered separately or combined on civil engineering structures as well as on historical buildings requiring implementation of proper repair methods.

This study aims to characterize the corrosion processes then the electrochemical chloride extraction (ECE) treatment in a both carbonated and chlorinated reinforced concrete. For this purpose, four series of specimens based on two cements and two aging processes were casted. In this paper the study's complete protocol is presented. First results obtained on one series of specimens during the aging then during the treatment are presented and discussed in a second time. SEM-EDS analyses and Raman microspectroscopy were used to characterize the corrosion product layer at the steel/concrete interface. SEM-EDS gave information about corrosion products distribution, morphology and elements of composition while Raman microspectrometry allowed the identification of crystallized corrosion phases formed. Electrochemical characterization (non-destructive-testing (NDT)) was used to follow the evolution of the state of corrosion of the rebar (active/passive).

## 2. Methodology

In this section the specimens' characteristics and the experimental program established to follow the evolution of corrosion state during the aging and during the electrochemical treatment are presented.

### 2.1 Specimens formulation and design

Design and composition of specimens used for this study must allow and facilitate chemical reactions within the concrete cover (high W/C ratio and limited vibration). To achieve this, cylindrical specimens of reinforced concrete of 10 cm in height and 4cm in diameter (Figure 1) were casted using the composition already used in Tong's thesis [1] that allows on a reduced scale to stay close to the granular distribution of a concrete (Table 1).

Table 1: "Micro-concrete" composition

siliceous Palvadeau aggregates (kg/m <sup>3</sup> )					Cement (kg/m <sup>3</sup> )	Water (kg/m <sup>3</sup> )	W/C ratio
0/0.315	0.315/1	0.5/1	1/4	2/4	387	251.55	0.65
159	295	192	686	229			

Two types of cement were selected:

- CEM I (52.5 N CP2; Holcim, Lumbres factory) is a usual Portland cement which will allow results comparisons. The specimens were named type 1.

- CEMIII/A (52.5 L PM ES CP1 NF; Lafarge, Le Havre factory), is a cement frequently encountered on concrete historical monuments. Furthermore, the use of this cement which contains blast furnace slag is promoted for the construction of new structures because of its lower impact on environmental issue (less CO<sub>2</sub> produced). Therefore, the results will help improve knowledge about the behavior of reinforced structure using this cement. The specimens were named type 3.

Rebar is a smooth round steel type S 235JR of 5mm in diameter with an active surface of 10cm<sup>2</sup>.

The open porosity measured after curing (28 days for CEM I cement and 90 days for CEM III cement) was about 18 % ± 1%.

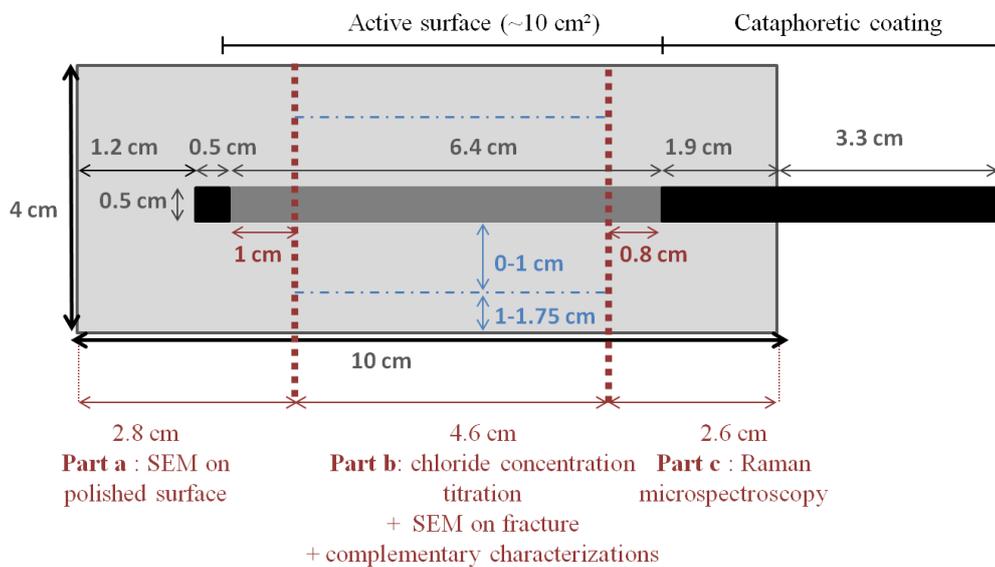


Figure 1 : Specimen design and decomposition for the analytical characterizations

## 2.2 Experimental set-up

A specific set-up was designed (Figure 2) in order to study, in a first step, the corrosion of a both carbonated and chlorinated reinforced concrete and then, in a second step, the efficiency and impact of the electrochemical repair (during the treatment and after its end).

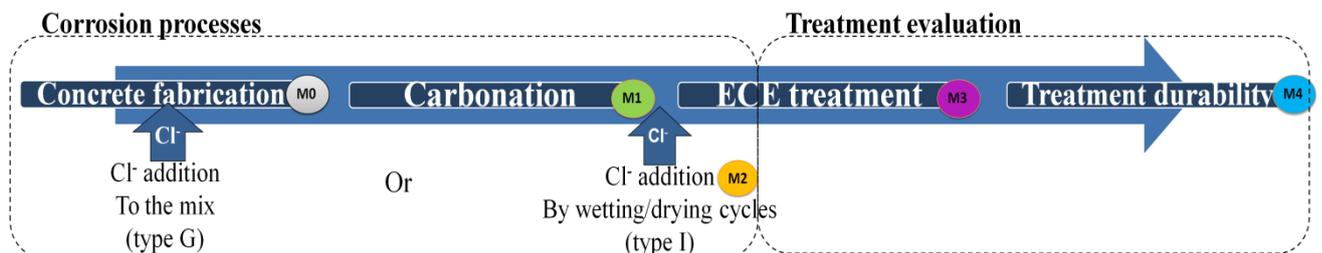


Figure 2 : Experimental set-up

Two different aging procedures were studied:

- Chloride addition to the mix (5 % of cement mass of NaCl) (M0) and then carbonation until complete carbonation of the concrete cover (50 % CO<sub>2</sub>; 70 % HR) (M1). The specimens were named type G.
- Carbonation until reaching the concrete/steel interface (50 % CO<sub>2</sub>; 70 % HR) (M1) and then chloride penetration by wetting/drying cycles (five days in a solution of 35 g/L NaCl and two days in the laboratory at room temperature) (M2). The specimens were named type I.

Evolutions of carbonation and chloride contamination by wetting/drying cycles were followed thanks to colour indicators, respectively phenolphthalein (0.5 % in ethanol which is not a CMR reagent at this concentration) and silver nitrate solutions (0.1 N).

After the aging step, the electrochemical chloride extraction treatment was then conducted on 37 specimens of each series (G1, I1, G3 and I3). The treatment principle is presented on Figure 3. As indicated in the NF EN 14038 part 2 standard [2], a current density of 1A/m<sup>2</sup> of steel was applied between the rebar and a titanium/platinum grid (counter-electrode) during 8 weeks. The electrolyte used was a disodium tetraborate solution (25g/L of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 10H<sub>2</sub>O) to promote ionic exchanges and facilitate chloride ions entrapment. The treatment monitoring was performed controlling and/or following the room temperature, the applied current, the voltage of each specimen and the voltage of the whole specimens on a one hour frequency base. Three control specimens were taken from the treatment after 3, 7, 14, 28 and 56 days, 56 days corresponding to the end of the treatment. These times were selected as several authors observed that the extraction of chloride ions is more efficient during the treatment's beginning [3-6]. Electrolyte was renewed at each term (except 3 days) to avoid a loss of treatment efficiency due to the increase of chloride ions concentration into the electrolyte. Regarding the chloride extraction evolution, concrete's free and total chloride concentrations were measured on two of the control specimens by AgNO<sub>3</sub> potentiometric titration (on the first centimetre around the rebar and on the 0.75 cm of external cover). Moreover the electrolyte chloride titration was also performed. Phenolphthalein test was performed on the surface of part c (Figure 1) of the two same control specimens. The third control specimen was kept to perform an electrochemical characterization after depolarisation.

After treatment, the electrochemical characteristics of the reinforced specimens will be checked every month to verify rebars are depolarized (storage at 60%HR and 20°C). Then cycles of relative humidity will be performed electrochemical characteristics followed to ensure the durability of the treatment.

Simultaneously to the treatment, two specimens (which are not submitted to the current) were used to observe lixiviation phenomenon. They were immersed in the tetraborate solution and Cl<sup>-</sup> titration was performed after 28 days and 56 days of treatment.

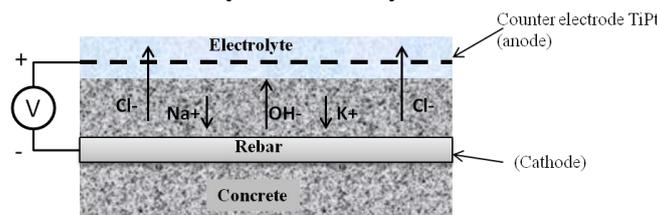


Figure 3 : Simplified principle of electrochemical chloride extraction

### 2.3 Analysis means

To study the corrosion process of the rebar, three main analyses means were used on different parts of the cylinder (Figure 1):

- A Jobin-Yvon Horiba (LABRAM) Raman spectrometer was used. Spectra were obtained with a helium-neon red laser (0.1 mW for these measurements). For these study acquisitions a x50 objective was used to focus laser light and collect spectra for duration of 600 seconds. Specific designed cells were prepared from the regular one after the aging step to follow the concrete/steel interface “in-situ” during the corrosion initiation and propagation and then during the treatment by Raman microspectroscopy. After cutting as presented Figure 1, a thin glass slide was pasted on the polished surface to isolate the steel/concrete interface from a direct contact with the external environment. After preparation, these samples were immersed in a 25g/L Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 10H<sub>2</sub>O solution. Regular observations at a magnification of 50 were made until the detection of pitting corrosion. Raman spectra were then acquired in different areas of interest. The same areas were followed during the ECE treatment and after treatment.
- A JEOL 5600LV scanning electron microscope (SEM) equipped with a micro-analyzer X in dispersal of energy Oxford Link Pentaflet was used to observe corrosion at the concrete/steel interface. Two types of samples were examined: polished cross sections to evaluate corrosion layers evolution and fractured samples to observe both corrosion crystallised phases' morphology and eventual modifications of the cement matrix.
- An electrochemical characterization was performed with a VMP2Z potentiostat (5 pathways) at each step of the process. The half-cell potential ( $E_{\text{corr}}$ ), the linear polarization resistance (LPR) and the electrical concrete resistance ( $R_e$ ) were measured and the corrosion rate  $i_{\text{Corr}}$  ( $\mu\text{A}/\text{cm}^2$ ) was calculated according to the formula (1).

$$i_{\text{Corr}} = \frac{B}{R_p S} \quad (1)$$

With:  $B = 26$  mV,  $R_p$  (ohm) the linear polarization resistance and  $S$  ( $\text{cm}^2$ ) the active steel surface ( $10 \text{ cm}^2$  in this study)

## 3. Results and discussion

In this section results obtained on G1 specimens casted with CEMI cement and NaCl addition to the mix and then carbonated are presented.

### 3.1 Corrosion processes

#### Corrosion products characterization

- Raman Spectroscopy

Trials of corrosion in-situ following were made on a specimen type G1 before carbonation. Chlorinated green rust (Figure 4) was the predominant phase found (main Raman bands at  $434 \text{ cm}^{-1}$  and  $506 \text{ cm}^{-1}$  and a chloride presence characteristic band around  $320 \text{ cm}^{-1}$ ) [7] which evidenced the presence of chloride into the corrosion processes. Moreover, green rust oxidation into FeIII oxyhydroxyde did not occur which proved the good isolation of the interface from a direct exposure to oxygen from the air.

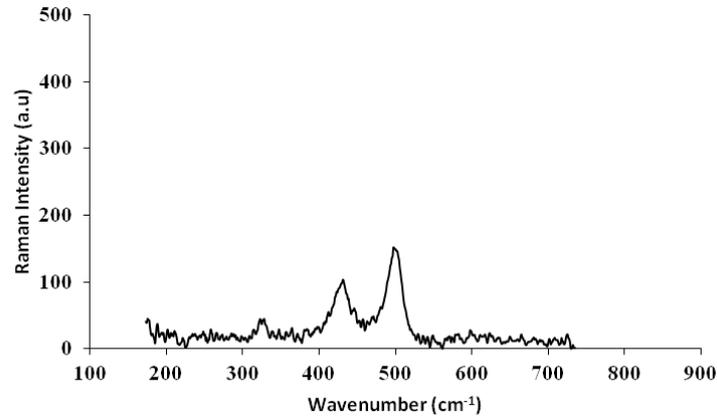


Figure 4 : Chlorinated green rust Raman spectrum

- Scanning electron microscopy

After casting, the steel/concrete interface was mostly characterized by an absence of corrosion (Figure 5-a). Figure 5-b shows a representative area of the interface after carbonation with about 5  $\mu\text{m}$  of corrosion products on the steel and 5  $\mu\text{m}$  migration within the concrete. After carbonation, the corrosion layer thickness could vary from 5 to 20  $\mu\text{m}$  and if the penetration of corrosion products within the concrete was mostly of 5 to 15  $\mu\text{m}$ , it could reach up to 250  $\mu\text{m}$  in few areas. The observation on fracture after carbonation (Figure 6-a) showed numerous areas of corrosion in the rebar print. The crystallisation morphology of corrosion products mainly containing Fe, O and Cl is presented on Figure 6-b.

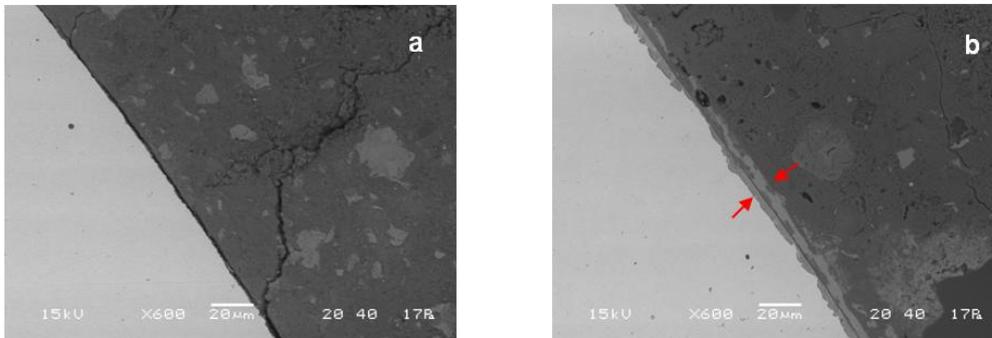


Figure 5 : BEIC-SEM images (x600) of the steel/concrete interface on cross section of specimens type G1, after casting without evidence of corrosion (a) and after carbonation with a thin layer of corrosion products (b)

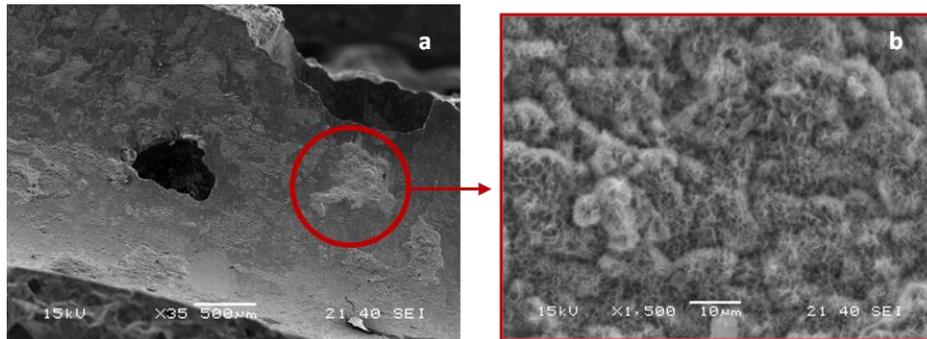


Figure 6 : SEI-SEM images of corrosion products observed into the rebar print on fracture after carbonation x35 (a) and x1500 (b)

### Electrochemical characterization

Fig 7, 8, and 9 respectively present the half-cell potential, the resistance and the corrosion rate of the G1 specimens at two different times. M0 is related to the corrosion state after curing (+3 days) while M1 is related to the corrosion state after carbonation (24 weeks after curing including a month of preconditioning and 14 weeks of accelerated carbonation).

From Fig 7, G1 specimens potentials measured after curing were in the range -230 mV to -579 mV with a mean value of -457 mV and a standard deviation (based on the 70 samples) of 84 mV while after carbonation, the average value and the standard deviation were respectively -550 mV and 14 mV (based on 57 samples). This indicates that after carbonation, the potential specimen values became more electronegative and more homogeneous.

From Fig 8, the average value and the standard deviation of the resistance were respectively 193 ohm and 16 ohm after curing and 97 ohm and 13 ohm after carbonation. The decrease by a 2 factor is rather unexpected as the carbonation process induces a reduction of the porosity. However both values (at M0 and M1) are still very low (some hundreds) and usually a significant evolution for the reinforced concrete is rather a thousand.

Finally, the corrosion rate after curing (Figure 9) was below  $0.1 \mu\text{A}/\text{cm}^2$  thus indicating a negligible level of corrosion according to the Rilem [8]. After carbonation a drastic increase of corrosion rate (values higher than  $10 \mu\text{A}/\text{cm}^2$ ) demonstrated a high level of corrosion [8].

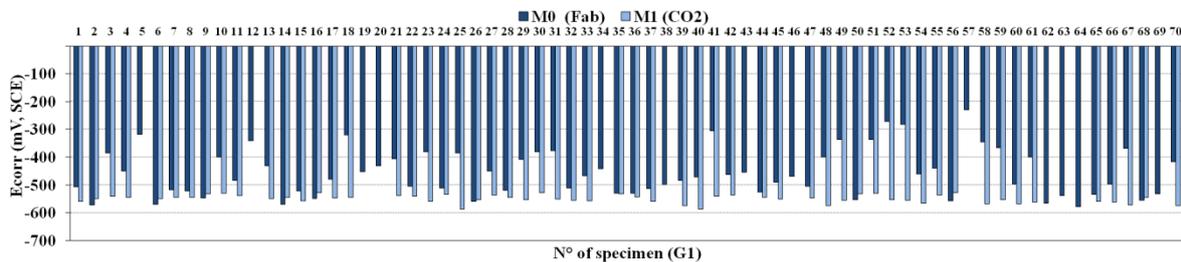


Figure 7 : Half-cell potential of G1 specimens after curing (M0) and after carbonation (M1)

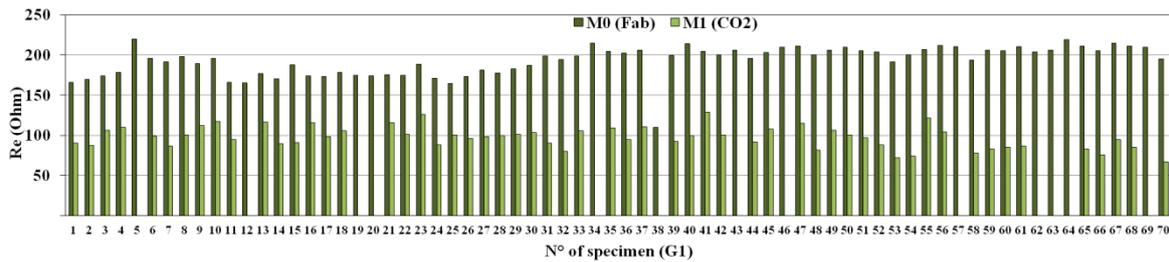


Figure 8 : Resistance of G1 specimens after curing (M0) and after carbonation (M1)

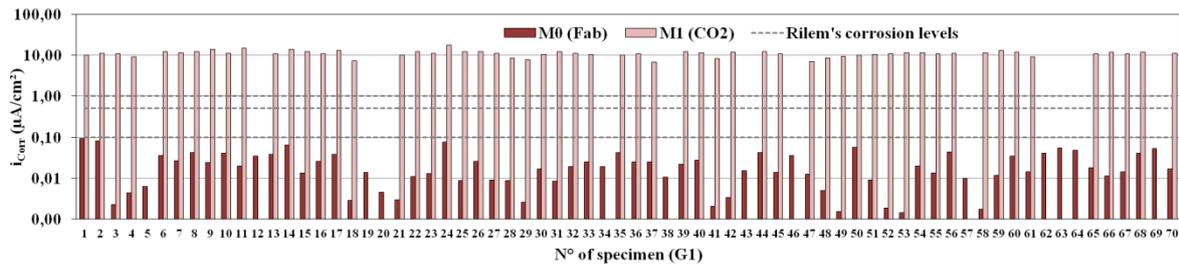


Figure 9 : Curent density of G1 specimens after curing (M0) and after carbonation (M1)

### 3.2 Electrochemical treatment on G1 specimens

ECE treatment implies several phenomena particularly corrosion products transformations, chloride ions extraction,  $\text{OH}^-$  formation and ionic migration. This part aims to study these different effects.

#### Corrosion products characte rization

##### - Raman Spectroscopy

During ECE treatment, regular Raman acquisitions (every day) were performed to follow the phases transformations induced. After two days of polarization, the main phase detected was magnetite (main Raman band at  $670 \text{ cm}^{-1}$ ) (Figure 10). This phase remained stable during 2 weeks of polarization after which the treatment was ended. Further experimentations will be done for a Raman microspectroscopy following of a specimen both chlorinated and carbonated.

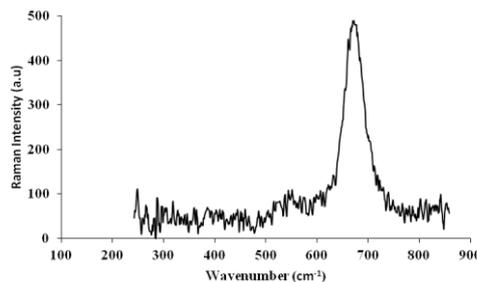


Figure 10 : Magnetite Raman spectrum

##### - Scanning electron microscopy

SEM observations and EDS acquisitions will be performed at the end of the treatment (not presented in this paper).

### Chloride titration

Figure 11 shows the evolution of chloride concentration during the ECE treatment as well as the alkaline evolution at the rebar level. The chloride threshold for preventing corrosion on new structures from the EN206 standard [9] has also been added.

Regarding the chloride extraction, the evolution of chloride ions extraction was in good agreement with the increasing chloride ions concentration titrated into the electrolyte. After 3, 7, 14 and 28 days the chloride ions extraction was respectively of about 52 %, 67 %, 89 % and 92 % in the external cover and 27 %, 70 %, 92 % and 96 % in the first centimetre around the rebar. The extraction was faster during the seven first days of treatment which is in accordance with literature results [3-6]. Results show that the free chloride concentration became less than the EN206 chloride threshold of 0.4 % mass of cement after 7-14 days of treatment. Figure 11 also highlights that the difference between total and free chloride ion concentrations decreased with the duration of treatment which could mean that bounded chloride ions can be electrochemically extracted.

Regarding the pH evolution (Figure 11), observed realkalisation was probably due to the hydroxyl ions formation around the rebar and the cations migration towards the rebar. Based on results obtained and the standard [10], concerning realkalisation the minimum treatment duration required is either 28 days to obtain a 10 mm realkalised concrete zone around the rebar or a range of 7 to 14 days considering the experimental rebar diameter (5 mm).

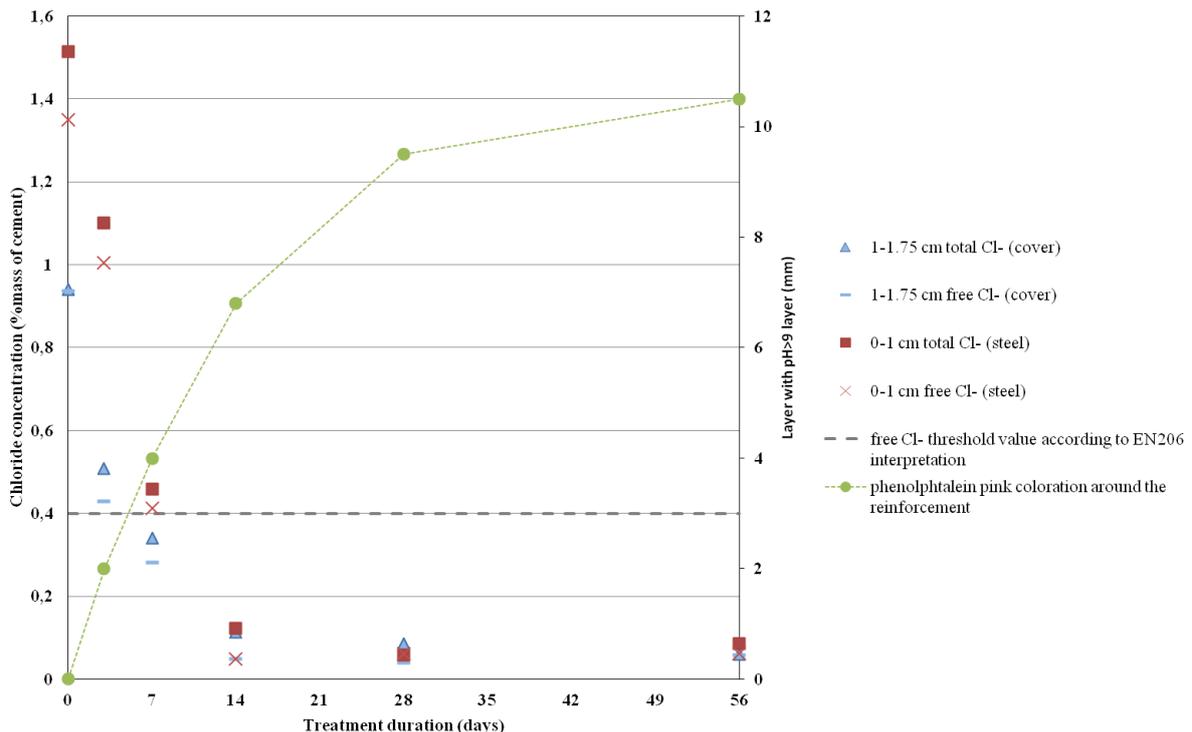


Figure 11: Evolution of chloride concentration and layer thickness (pH>9) during ECE treatment

#### 4. Conclusion

In this experimental work, the set-up design adopted to study, first the corrosion process on both chlorinated and carbonated reinforced concrete specimens, and second, the electrochemical cathodic treatment were presented.

First results obtained on G1 specimens allowed to establish the following conclusions:

- Chloride contaminated G1 specimens showed a negligible corrosion 30 days after curing as indicated by corrosion rates less than  $0.1 \mu\text{A}/\text{cm}^2$ .
- After the carbonation process, as expected, corrosion increased rather drastically as evidenced by corrosion rates higher than  $10 \mu\text{A}/\text{cm}^2$ . SEM results confirmed this behaviour with the observation of corrosion products on most of the interface (5-20  $\mu\text{m}$  on the rebar and up to 250  $\mu\text{m}$  of penetration within the concrete).
- Efficiency of the electrochemical treatment based on chloride extraction as well as realkalisation of the concrete around the reinforcement was demonstrated. Two weeks of treatment were needed to obtain a CI concentration below the threshold value of 0,4 % mass of cement while 28 days of treatment lead to one centimeter of realkalisation.

The following of treatment durability and Raman spectroscopy results will complete the experimental work on G1 specimens. Comparison with 3 other types of specimens will give a larger view on this subject.

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