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Electrochemical chloride extraction: efficiency and side effects

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Abstract

Some specimens of reinforced concrete cast with an alkali-resistant aggregate, previously maintained in a solution of NaCl, were subjected to an electrochemical chloride extraction (ECE). The chloride profiles before and after treatment were determined. Likewise, alkali ions profiles before and after treatment were determined. After treatment, some specimens were stored in a controlled atmosphere (60 °C and 100% RH) in order to accelerate the alkali–silica reaction, if any.

Results of chloride content after treatment show that about 40% of the initial chloride is removed within 7 weeks. About one-half of the chloride close to steel was removed, but at the same time, significant amounts of alkali ions were observed around the steel.

Microstructural observations by scanning electron microscopy (SEM) showed that after treatment, new cementitious phases containing higher concentrations of sodium, aluminum and potassium were formed. Moreover, alkali–silica gel was observed in the specimens stored at 60 °C and 100% RH. It may be possible that the ECE accumulates locally high amounts of alkali ions that stimulate the alkali–silica reaction even though the concrete contained nominally inert siliceous aggregates. The specimen expansions were not recorded, but no cracks were observed.

Keywords: Electrochemical chloride extraction; Corrosion; Microstructure; SEM

1. Introduction

Corrosion of embedded steel in concrete represents a great concern in relation to the durability of reinforced structures. Generally, the steel in hardened concrete is protected by a passivating film. However, the presence of sufficient chloride ions, or carbonation, causes the passivating film to break down. Therefore, steel is no longer protected against corrosion in the presence of moisture and oxygen.

Various protective methods, including epoxy-coated steels, overlays, membranes, impregnation or inhibitor, are used to prevent corrosion in new structures. For old structures, the conventional repair technique consists in locating the corroding areas through the potential mapping technique, determining the chloride content in corroding and passive zones and removing the chloride-contaminated concrete. However, conventional patch repairs have not generally proved to be a lasting solution to this type of deterioration because of the difficulty of effectively removing chlorides from all parts of the structure.

One specific method for rehabilitating the deteriorating reinforced concrete consists in extracting the chlorides from concrete by electrochemical means. This process is known as "electrochemical chloride extraction" (ECE) or "desalination". The technique involves the application of a high current density (DC) for a short period, typically a few weeks. The steel reinforcement acts as the cathode, and an extended anode is placed in a suitable electrolyte at the concrete surface. The positive terminal is connected to the secondary anode and the negative terminal to the steel. When the negative terminal of the DC power source is connected to the steel, the steel achieves negative polarity; it repulses anions and attracts cations present in the concrete pore solution; the cations and anions present in the concrete pore solution act as the electrolyte that permits movement of current between the anode and the cathode. Therefore, accumulation of sodium, potassium and hydroxyl ions occurs at the cathode. This accumulation has been shown to increase the risk of alkali–silica reaction in concrete containing potentially reactive aggregates [1].

Recent studies suggest that even prolonged treatment would remove only 40–55% of the total chloride [2–4]. This investigation determines the reduction in chloride content, measures accumulation of cations near the steel

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Table 1
Chemical analyses and Bogue composition of cement used

	CaO	SO_3	SiO_2	Al_2O_3	MgO	Fe_2O_3	Na_2O	K_2O	Na_2O_{equiv}	C_3S	C_2S	C_4AF	C_3A
CEM I 52,5R PM ES	67.2	2.10	22.7	2.9	0.71	2.00	0.29	0.10	0.35	70.7	12.6	6.8	4.3

surface and analyzes the effects of the applied electric field on the microstructure of concrete.

2. Experimental procedures

Cylindrical concrete specimens (11-cm-diameter, 10-cm-long) were cast. The aggregates were constituted of silica, quartz and smaller contents of feldspars, micas and chlorites. These aggregates were taken from the French river ‘‘Garonne’’. According to the NF P 18–589 standard (chemical method), these aggregates are nonreactive in relation to the alkali–aggregate reaction, although some phases are sensitive to alkali. The chemical analyses of cement used and Bogue composition are given in Table 1.

A grooved steel of ordinary hardness (10-mm-diameter, 14-cm-long) was placed in the specimen during fabrication; it lay along the axis of each specimen, as illustrated in Fig. 1. Table 2 summarizes the concrete mix design.

The specimens were removed from the mold 24 h after casting and cured (20 °C and 50–60% HR) for 7 days and then subjected to cycles of immersion and drying: immersion in the aggressive medium (water with 35.5 g/l NaCl) and drying at 40 °C in order to accelerate penetration of chloride ions. The ECE was applied after approximately 10 months, when all concrete specimens contained a rather significant quantity of chloride.

An externally derived cathodic current was applied between the steel of each specimen [immersed in the saturated $Ca(OH)_2$ solution] and a titanium mesh anode. A cathodic current density of 1 A/m^2 of steel surface was applied for 50 days. The circuitry arrangement for the current supply used in this work is shown in Fig. 1. Constant current density was kept in each specimen by adjusting a variable resistor connected to the specimen in parallel. Another resistor, of 1 Ω, connected in series with the specimens, allowed us to measure the current imparted to the steel.

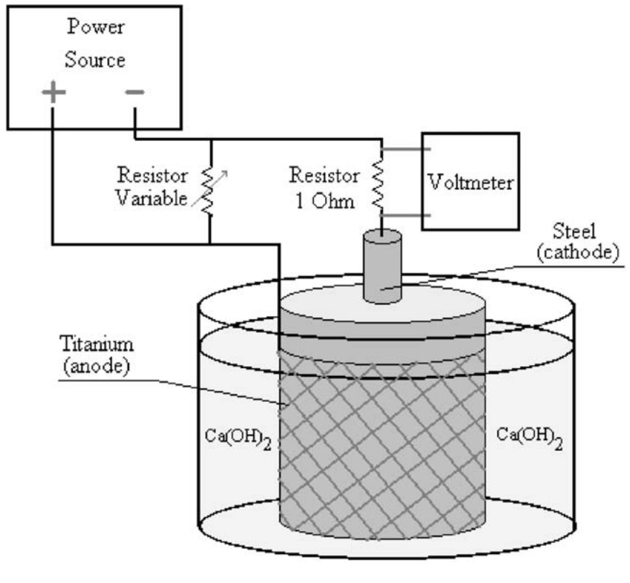

Fig. 1. Circuitry arrangement for the ECE treatment.

At the end of the treatment (after 50 days), some cores were extracted from both untreated and treated specimens, so as to measure the concentration profiles for Na^+, K^+ and Cl^- (total and ‘‘free’’) ions as a function of distance from steel. These specimens were cut in slices and later powdered. A chemical analysis was performed to determine potassium and sodium ions in concrete by dissolving the concrete powder with boiling water; the solution was analyzed through atomic absorption spectroscopy. Chloride concentration was determined through an acid extraction technique (total chloride) and water extraction technique (free chloride), by potentiometrically titrating with silver nitrate solution [18], pursuant to the AFREM recommendation (chemical method). In this work, the chlorides extracted by cold water are termed *free chlorides*.

The concrete and steel surfaces of some specimens were examined by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) to determine the microstructure of cement paste. The observations were compared with untreated specimens. Some treated specimens were stored under controlled environmental conditions (60 °C and 100% RH) in order to stimulate the alkali–silica reaction. After approximately 6 months, these specimens were retrieved for SEM.

3. Results

3.1. Migration of chloride ions

The results obtained from the chloride removal are given in Figs. 2 and 3. We can note that the free chloride content

Table 2
Concrete formulation

Siliceous sand	810 kg/m^3
Siliceous gravel	1000 kg/m^3
Cement CEM I 52,5	400 kg/m^3
Water	180 l/m^3
Water/cement	0.45
Compressive strength (28 days)	40 MPa

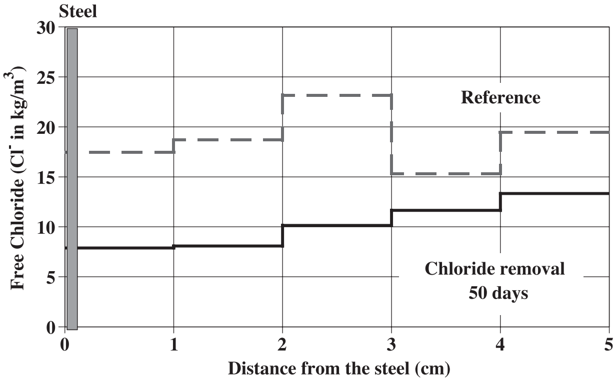

Fig. 2. Evolution of free chloride ions vs. distance from the steel.

before treatment near the steel was about 18 kg Cl^-/m^3 of concrete. After treatment values, up to 7 kg Cl^-/m^3 of concrete was found near the steel.

Based on free chloride content of control specimen, the average reduction in free chloride content near the steel was about 40%. The results obtained from total chloride removal indicate the same trend. The corresponding average reduction in total chloride adjacent to the steel was 40%.

3.2. Migration of sodium and potassium ions

Fig. 4 shows the concentration profiles of alkali ions (as $Na_2O_{equiv} = Na_2O + 0.658\ K_2O$). It can be seen that prior to treatment, the alkali ion content was about 12 kg Na_2O_{equiv}/m^3 of concrete. This high concentration is due to the introduction of Na^+ during the immersion–drying cycles.

After treatment, a higher concentration of alkali, 27 kg Na_2O_{equiv}/m^3 of concrete, was found near the steel, as expected.

3.3. Visual inspection

Before treatment, the concrete cover of control specimens was removed in order to inspect the condition of the steel, which was substantially corroded in the chloride-contaminated concrete.

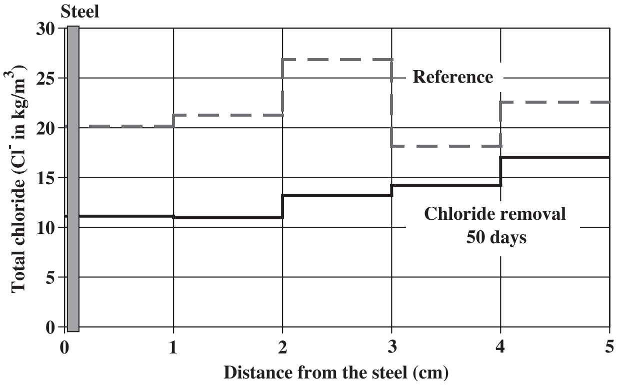

Fig. 3. Evolution of total chloride ions vs. distance from the steel.

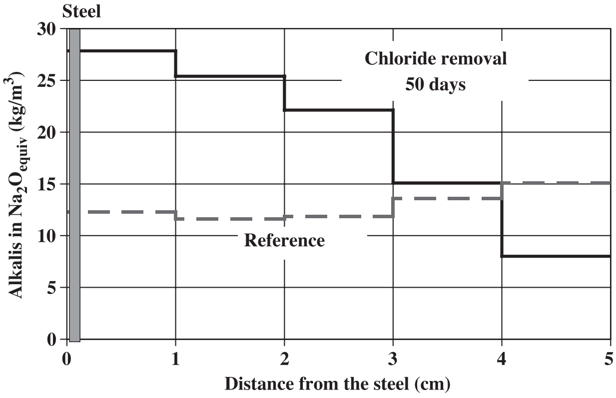

Fig. 4. Evolution of alkali ions vs. distance from the steel.

After treatment, similar amounts of corrosion products were found in the steel of the control specimens. However, one “slight white deposit” was observed on the surface of steel.

3.4. SEM of the concrete and the steel surface

The steel and concrete surfaces taken from treated and untreated specimens were examined by SEM. Untreated specimens showed the typical cement paste morphology composed of calcium silicate hydrate and calcium hydroxide crystals (Figs. 5 and 6).

Immediately after treatment, a thin layer of fine granular mortar paste was observed on steel surfaces (Figs. 7, 8 and 9). EDS analyses revealed the presence of Ca, K, Na and Al (Fig. 10).

At the concrete–steel interface, sodium-rich crystals with a well-defined morphology were observed (Figs. 11 and 12). They looked like “small canes”. In addition, another sodium-rich phase was observed around the steel (Figs. 13 and 14).

The specimens stored for 6 months at 60 °C and 100% RH were examined by SEM. Two phenomena were noted:

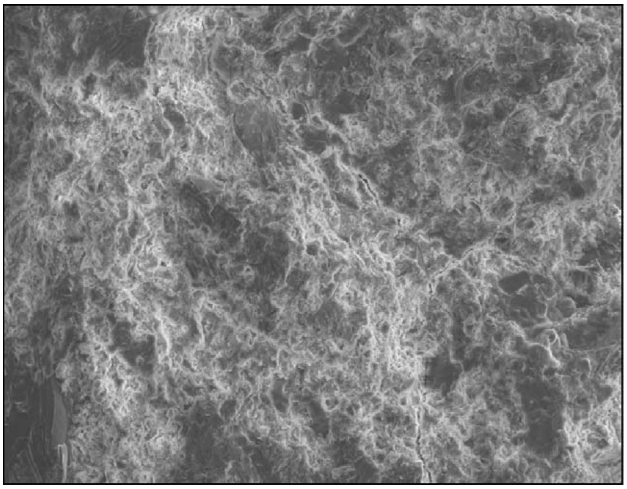

Fig. 5. Typical cement paste morphology (× 400).

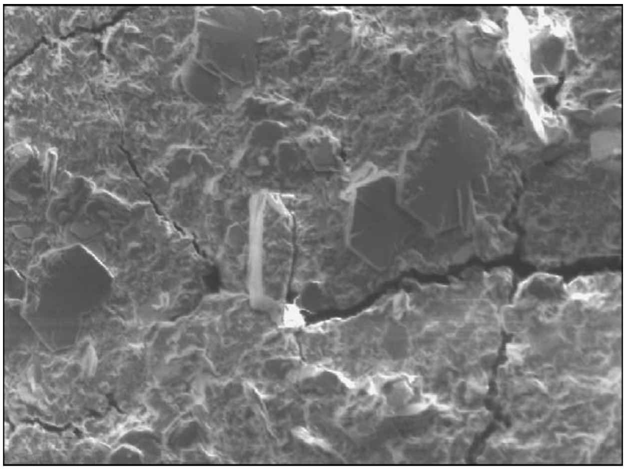

Fig. 6. Calcium hydroxide crystals (× 400).

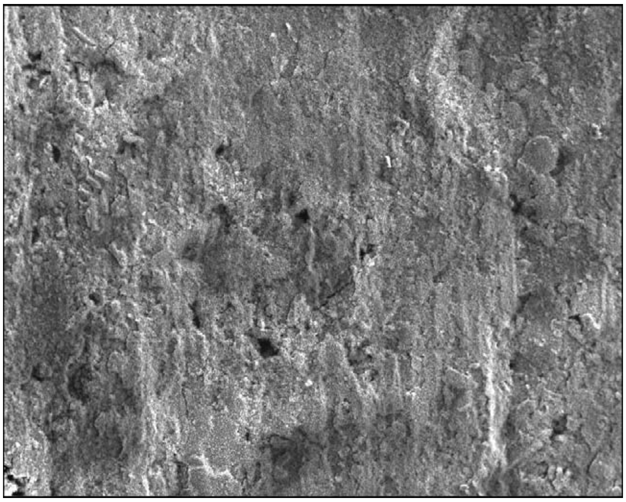

Fig. 7. Film developed on steel after treatment (× 400).

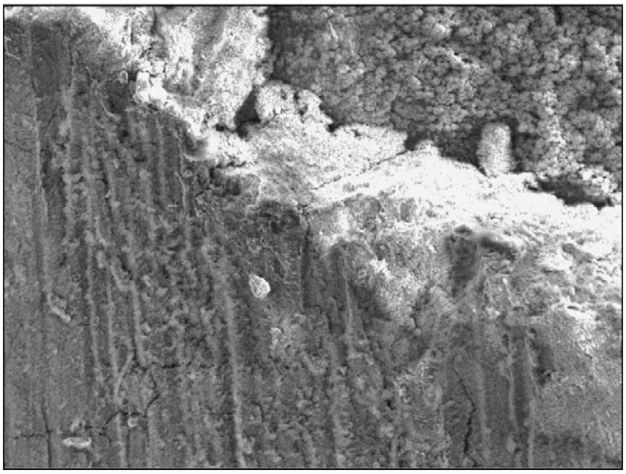

Fig. 8. Imperfections of film on steel (× 400).

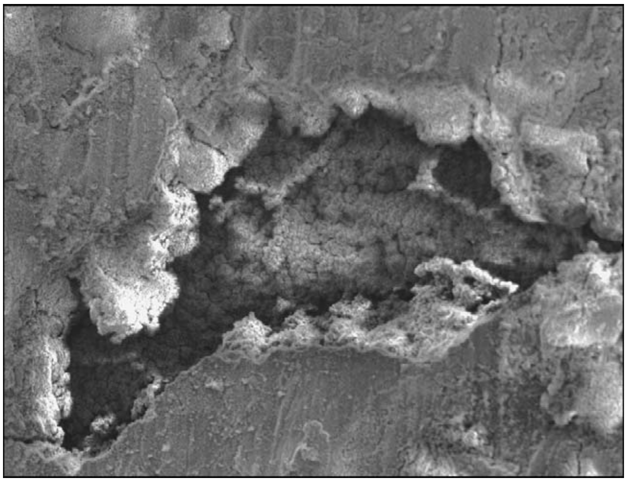

Fig. 9. Imperfections of film on steel (× 400).

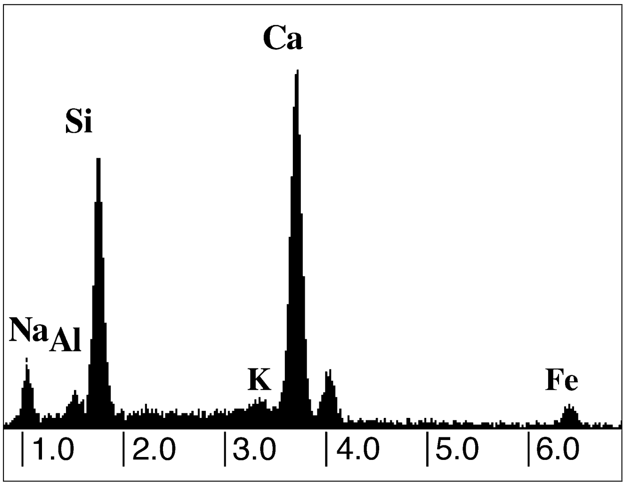

Fig. 10. EDS analyses of Fig. 7.

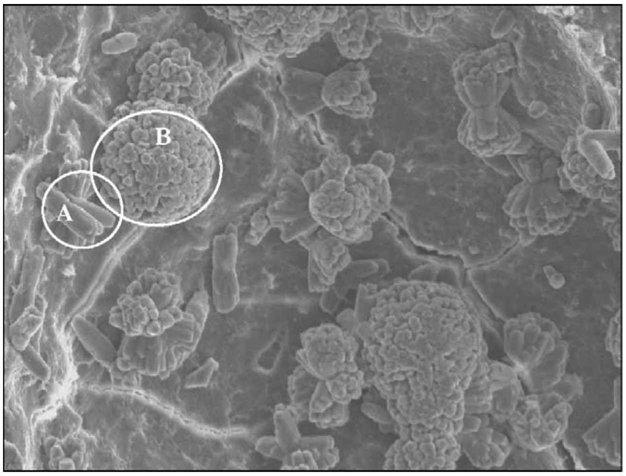

Fig. 11. Sodium-rich phases (× 2000).

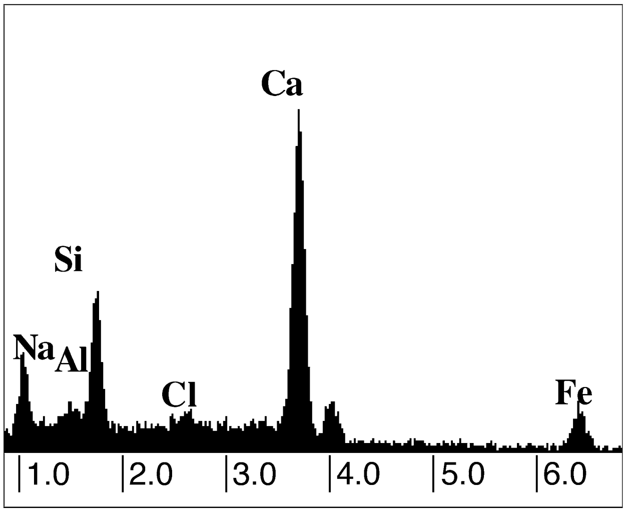

Fig. 12. EDS analyses of Fig. 11.

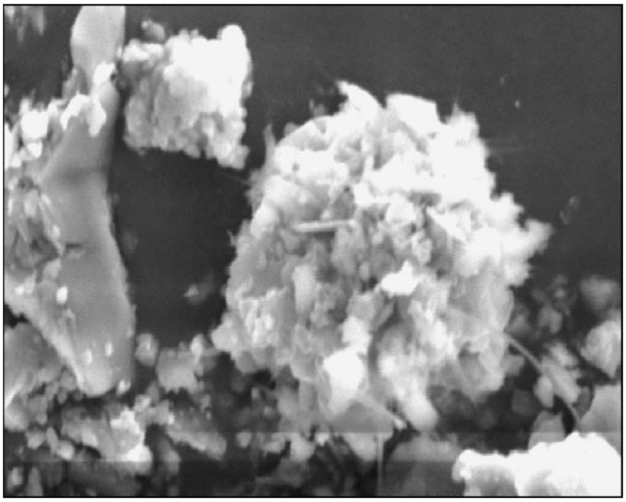

Fig. 13. Sodium-rich phases (× 4000).

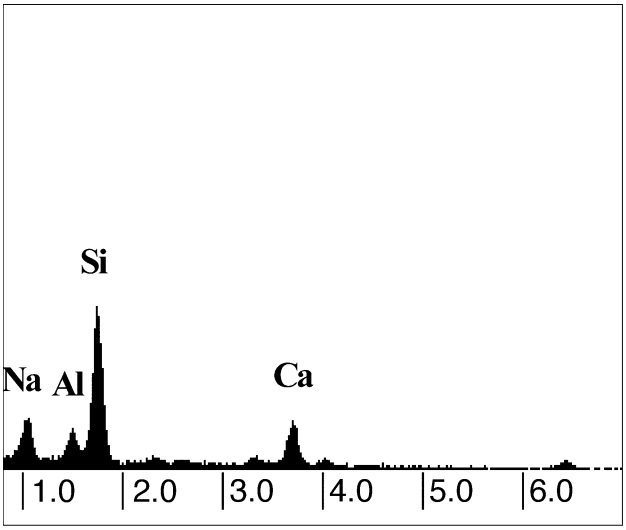

Fig. 14. EDS analyses of Fig. 13.

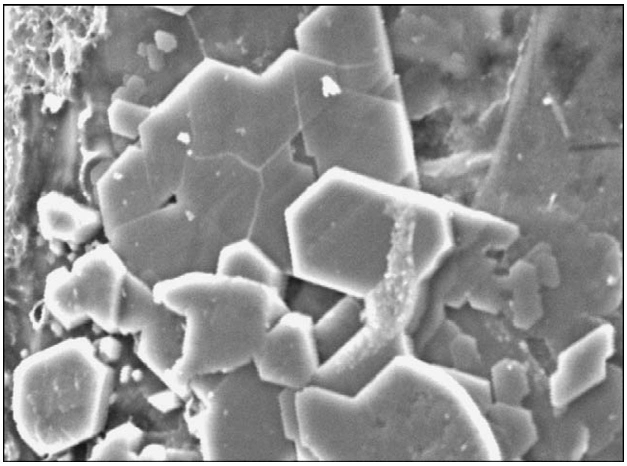

Fig. 15. Hexagonal plates on the steel–concrete interface (× 3000).

first of all, the formation of hexagonal plates at the steel–concrete interface (Figs. 15 and 16) and secondly, the formation of alkali–silica gel (Figs. 17 and 18).

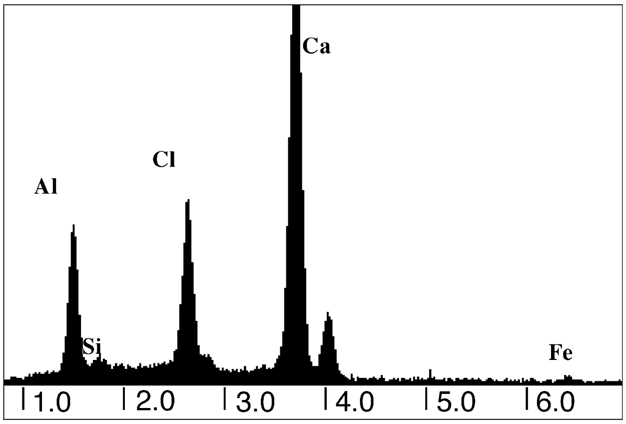

Fig. 16. EDS analyses of hexagonal plates of Fig. 15.

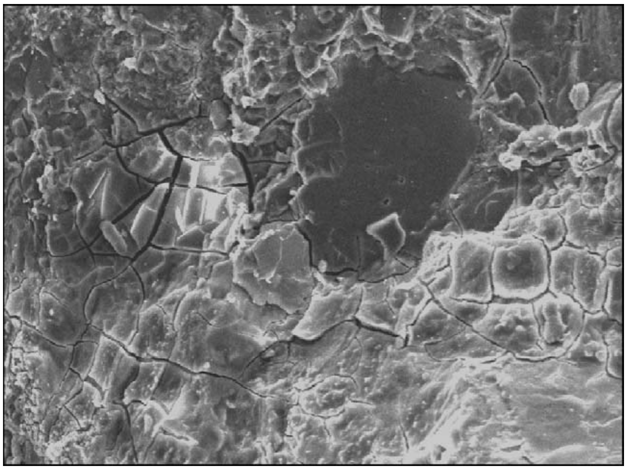

Fig. 17. Alkali–silica gel (× 1000).

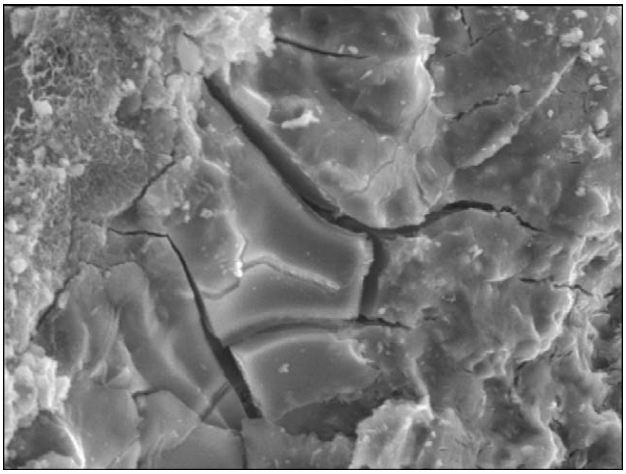

Fig. 18. Alkali–silica gel (× 3000).

With regard to the hexagonal plates, EDS analyses indicated the presence of Ca, Al and Cl elements (Fig. 16). Friedel's salt shows a typical hexagonal plate-like morphology [5] or spherulite morphology [6,7]. This led us to conclude that Friedel's salt was "re-formed".

It has been disclosed in previous papers that the cathodic polarization of steel in concrete may induce the formation of alkali–silica gel in concrete containing potentially reactive aggregates [1,14]. The acceleration of ASR in the ECE may be due to the electromigration of Na^+ and K^+ ions from the surrounding matrix towards the steel and the subsequent formation of OH^- ions due to the cathodic reaction.

In this work, alkali–silica gel was observed in specimens made without reactive aggregate (these are not subjected to alkali reactivity in accordance with standards like NF P 18–589). In fact, these aggregates are made with a majority of nonreactive aggregates and a minority of potentially reactive phases. However, no cracks were observed at the specimen surface.

4. Discussion

4.1. Layer observed on the steel

As observed in our study, formation of a white deposit on the steel surface after chloride removal treatment has already been noticed by others [8–10]. Thus, Batic et al. [8] observed a thin layer of fine granular mortar paste surrounding the steel in mortar specimens subjected to cathodic protection. They concluded that the composition of this layer differed from bulk mortar, containing 50 ± 5% of quartz material and had a calcium oxide/silica ratio lower than that of the original cement. On the other hand, it has been postulated that the presence of a calcium hydroxide-rich layer on the steel surface is the major factor inhibiting corrosion initiation of steel in chloride-contaminated concrete [9]. Glass and Buenfeld [9] reported that the formation of a $Ca(OH)_2$ layer on the surface steel increases its tolerance to chlorides. They concluded that increasing the tolerance to residual chloride by forming a calcium hydroxide-rich layer at the steel surface may represent a decisive factor in the success of the treatment even if a significant quantity of chloride remains in the concrete after treatment (in our work, 12 kg Cl^-/m^3 of concrete). Furthermore, Glass and Buenfeld [9] suggest that electrochemical treatment (removal chloride or cathodic protection) could also be applied as a preventive measure to limit the risk of corrosion initiation at a poorly compacted steel–concrete interface. Indeed, it has been postulated that the quality of steel–concrete interface has a major influence on the prediction of corrosion onset in relation to chloride content [17].

In the title study, visual observation of the surface steel revealed no significant changes when treatment was applied (except for the white deposit), and it is possible that at high degrees of corrosion, repassivation of steel is not possible even if the electrochemical chloride removal is applied and a calcium hydroxide-rich layer is formed. Electrochemical measurements are carried out to determine whether the calcium hydroxide-rich layer is able to induce the repassivation of the steel over corrosion.

4.2. Alkali migration and formation of new phases

The cations and anions present in the concrete pore solution act as the electrolytic medium for the movement of current. The negatively charged ions (particularly the chlorides) are thus extracted as they migrate towards the external anode. At the same time, the alkali metal ions migrate towards the steel where they accumulate and react with the hydroxide ions produced by the cathodic reactions. It is assumed that the consequence of alkali metal ions migration towards the steel is that they tend to electro-diffuse "heavily solvated" with a sheath of water molecules [10]. Furthermore, the accumulation of cations may also cause harmful chemical changes in the concrete; formation of sodium-rich (with a fine spherulite structure), calcium-rich and potassium-rich phases has been reported [11].

In addition, Marcotte et al. [11] showed the formation in steel–concrete interface of phases very similar to those illustrated in Fig. 11. However, these researchers claimed that the phases observed were iron-rich and concluded that the formation of these iron-rich plates could probably result from the electrochemical reduction of iron corrosion products during the extraction treatment. The title study shows crystals extremely similar to those observed by Marcotte (crystals A and B). There is some evidence that in the vicinity of the reinforcement, both free chlorides and a proportion of bound chlorides are removed [2,16]. Thus, a new recrystallization of Friedel's salts is possible. In addition, Lea [12] revealed that the free chloride ions are in equilibrium with the chloroaluminate compounds. Thus, the depletion of free chloride ions during extraction treatment can cause a breakdown of chloroaluminates, releasing chloride ions. It is obvious that chloride-rich, aluminum-rich and calcium-rich crystals shown here were formed because of the reequilibrium between free chloride and bound chloride ions.

It is interesting to mention that the phases observed in this work are not related to the U phase observed in some works [19], because of special conditions for its formation, requiring high contents of alkalis and sulfates [20].

Regarding the formation of the alkali–silica gel, researches have pointed out that chloride removal treatment may accelerate the alkali–silica reaction. This acceleration may be due to the electromigration of Na^+ and K^+ ions from the surrounding matrix towards the steel, but its mechanism is not fully understood.

Investigations have been carried out in order to resolve this issue [13–15]. The results are varied; Natesayer [1], who used reactive siliceous aggregates, alkali contents from 0.95% to 2.8% and current densities in the range of 0.40–130 mA/m^2 for 24 months periods, has not observed any significant differences in expansion between treated and untreated specimens.

Page et al. [14] claimed that a galvanostatic polarization at 20 mA/m^2 for a 800-day period in concrete containing reactive aggregates and a bulk alkali content of 25 kg Na_2O_{equiv}/m^3 of concrete did not cause any expansion sufficient to initiate extensive cracking. However, Page et al. observed that for specimens subjected to potentiostatic polarization at -850 or -700 mV (vs. SCE), the expansions produced were sufficient to cause extensive cracking of the concrete. Page and Yu [15] ensured that for concrete specimens containing potentially reactive aggregates and alkalinity below the level required to induce the alkali silica reaction, local expansion and cracking in the vicinity of steel cathodes may be caused by the application of current densities in the range 1–8 A/m^2 for periods of 4–12 weeks and subsequent moist storage. An interesting point mentioned by Page and Yu [15] is that the highest expansions were recorded in the cases of specimens treated at an intermediate current density of 3 A/m^2. To explain these results, the authors concluded that there is a “pessimum effect” in the relationship between expansion and total charge passed during electrolysis ($1-2*10^7$ C/m^2). They speculated that the maximum expansion could be attained for concrete with specific ratios of equivalent Na_2O to reactive SiO_2 (this being maximized at an intermediate ratio of equivalent Na_2O/SiO_2). Thus, during treatment, the local concentration in alkali ions developed in the vicinity of the steel must increase with time of current application, and since the reactive SiO_2 content of a particular concrete is constant, ASR gel of a maximum expansion tendency may be formed at a critical value of the total charge passed (as stated by Page).

In previous researches [14,15], two points were highlighted: First of all, these works focused on the possible expansions of specimens after treatment. In our work, the expansion of the specimens has not been monitored, but no cracks were detected on specimen surfaces. Secondly, in order to adjust the total alkali content close to the threshold level required to generate ASR, NaOH was added to the mix water. These alkali ions can be chemically bound, therefore, they will not contribute to ASR. In our study, the conditions required for ASR were present: (1) high amount of alkali ions coming from the environment (NaCl) were accumulated around the steel due to cathodic polarization; (2) some reactive aggregates are in accordance with standards; (3) hydroxyl ions formed on the steel can react and dissolve the reactive silica. Considering the results found in this work, it seems obvious that the formation of alkali–silica gel was restricted by deficiency of available silica.

5. Conclusions

Electrochemical chloride removal was applied on concrete specimens in order to verify the effectiveness of the treatment and the possible formation of new phases in both concrete and steel–concrete interfaces.

The treatment reduced the content of chloride by 40–45%; however, an accumulation of alkali ions was observed around the steel. Microstructural analyses by SEM revealed the formation of sodium-rich phases, the presence of a thin cementitious layer surrounded the steel and a recrystallization of Friedel’s salt on steel–concrete interface. Finally, the formation of alkali–silica gel was only observed in specimens kept in accelerated conditions (60 °C and 100% RH). This suggests that “little or no” potentially reactive aggregate may actually become reactive as a result of increased hydroxyl ion content arising from electrochemical treatment.

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