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Efficiency of the Electrochemical methods for the repair of reinforced concrete structures

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Abstract

The aim of this thesis is to obtain information on the efficiency of electrochemical chloride removal, as a restoration technique for chloride contaminated concrete are presented. Since they are much less costly and more friendly to the environment and to worker health than traditional repair methods. A series of highly important questions will be treated during the thesis namely:

- ✓ Is applying the electrochemical methods reduce the rate of the corrosion?
- ✓ Secondary effect of these methods on the RCS:
  - ➢ Is there a Possibility of initiation of the alkali silica reaction?
  - ➢ Can these methods change the mechanical behaviour of RCS?

Keywords: Concrete, repair, corrosion, electrochemistry

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1. Introduction

The deterioration of concrete structures due to the penetration of chloride is considered as one of the major problems in civil engineering. Structures built in an aggressive environment such as coastal regions and acid sulfated soils will be particularly attacked by these agents. Corrosion of reinforced concrete structures is a growing international problem. Several studies have identified corrosion of concrete steels as the main degradation mechanism of bridges [1-2-3]

Corrosion of concrete steel can damage or reduce the serviceability of concrete structures in several ways causing catastrophic disorders [4]. The first way is the corrosion caused by expansive products which generate tensile stresses in the concrete surrounding the reinforcing steel, which can cause cracking of the concrete [4-5]. Cracks can reduce the strength and stiffness of the concrete structure and accelerate the penetration of aggressive ions, leading to other types of deterioration of the concrete, which leads to further cracking. The second way is due to the fact that the corrosion products are very porous, weak and often form around reinforced concrete steel, which reduces its section and decreases the bonding force between steel and concrete. which decreases the ultimate load capacity and ductility of the structure [6].

Chloride can be introduced into concrete from internal (aggregate, water and admixture) and external (using salt as a de-icing agent or exposure to seawater) sources. i.e. as a contaminant in the original concrete mixture and resulting from an intrusion from the environment. In the event of internal contamination, if the chloride content of the interstitial solution around the concrete steel reaches the threshold value, the presence of chloride will immediately trigger the reprocessing of the concrete steel in the concrete. In the event of penetration of chlorides from external sources, the chloride content in the concrete will increase over time, which could possibly create a situation in which the concrete would no longer be able to protect the reinforcing steel from depassivating. [7]

The service life of concrete structures controlled by corrosion of concrete steel can be divided into two periods. The initiation period and the propagation period. The initiation period lasts from the start of the commissioning of a concrete structure until the point where the chloride ion concentration around the reinforcing steel in the concrete has reached the critical value for initiation corrosion. The propagation period can range from the onset of corrosion to the limit state of the concrete structure, beyond which the structure cannot be used safely without taking repair or restoration measures. The duration of the initiation period depends on the corrosion rate of the reinforcing steel. Usually, the penetration of chloride from an external source into concrete is a much slower process than the spread of corrosion. [8] Thus, the start-up period could be used to conservatively estimate the life of a concrete structure.

Corrosion of reinforcing steel in concrete is an electrochemical process which involves the transfer of electrically charged ions between two areas of the surface of reinforcing steel with different potentials (anode and cathode) through the interstitial fluid of concrete, which serves as an electrolyte. The corrosion rate of reinforcing steel in concrete depends on the ease of flow of ions participating in the electrochemical process. Various factors such as the electrical resistivity of concrete, the electrochemical potential of concrete steel, the availability of oxygen and humidity in the cathodic zone and the ratio of cathodic zone to anodic zone control the flow of charged ions. electrically in concrete. [9]

Now days, a significant investment in the repair of reinforced concrete structures is being studied due to the aggressiveness of the environment and aging of the concrete. In this perspective, several techniques of repair and rehabilitation of Concrete structures have been developed to optimize the cost and the efficiency of repair projects [10-11]. The conventional method of repairing an affected reinforced concrete structure by corrosion is based on the removal of concrete surrounding the rebar. Then, the oxides of the bar are cleaned, and a new layer of concrete or repair mortar is added, however Feedback has shown that these methods are not satisfactory solutions.

The interest of these electrochemical techniques which we are going to study, lays on the capacity to remove the aggressive agents while maintaining the covering of concrete and allowing the passivation of the reinforcement. We distinguish three methods according to the type of structure and the aggressiveness of the environment:

- Cathodic protection, [12,13]
- Electrochemical chloride extraction [14-17]
- Electrochemical realkalisation. [18.19]

Electrochemical maintenance method is characterized by the application of a temporal cathodic current to the steel connected as a cathode by means of an anode placed on the surface of the concrete.

The arrangement of these techniques improves the formation of hydroxyl ions at the rebar which supports the alkalinity of the aqueous phase near the rebar.

In our case we will be interested in the electrochemical Chloride extraction method since our study is based on the corrosion of reinforced concrete structures attacked by Chloride.

Description of the different degradation affecting the reinforced concrete structures

Carbonation of concrete

Definition

It is a chemical phenomenon that occurs on the surface of concrete and continues for years. During this reaction, lime hydrate and carbonic acid combine to form limestone, releasing water. Lime hydrate ($Ca[OH]_2$) comes from hardened cement paste where it is in solution in the pores. It reacts with the carbonic acid in the air to form insoluble lime ($CaCO_3$) which deposits in the pores. The water (H_2O) released by this reaction again dissolves lime hydrate from the cement paste, so that the reaction with carbonic acid in the air can continue.

The carbonation rate depends on many factors such as the quality of the concrete, water content, relative air humidity, temperature, etc. [20]

The mechanisms of carbonation

- Incubation phase

The reaction of (CO_2) from the air with alkaline substances in concrete is called carbonation. The combination of carbon dioxide with calcium hydroxide - calcium hydroxide also called portlandite is formed during the hydration reactions of cement gives rise to calcium carbonate, as shown in the reaction below: Ca (OH) $_2$ + CO_2 H_2O → $CaCO_3$ + H_2O This reaction only takes place in an aqueous medium. First, carbon dioxide has to dissolve in the pore water, which causes the pH to drop (from about 13 to 9). By this drop in pH, calcium hydroxide also enters into solution. The two products react and precipitate in the form of calcium carbonate. The relative humidity of the surrounding environment which determines the water content of the concrete is a fundamental parameter. Indeed, for the process to continue, a supply of fresh carbon dioxide is required. However, the diffusion of dioxide takes place 10,000 times faster in air than in water. The relative humidity must therefore be low enough for the diffusion of carbon dioxide to be possible, but it must also be high enough for the actual carbonation reaction, which can only be carried out in the aqueous phase, to take place.

The carbonation rate decreases over time. As the carbonation zone (carbonation front) progresses, the calcium carbonate formed gradually clogs the pores of the concrete. The CO2 has to travel a longer distance to find the alkaline substances, and therefore the process slows down. Carbonation is maximum when the relative humidity is between 40 and 70%, it then decreases quickly. Figure 2 gives the order of magnitude of the depth of carbonation that can be expected depending on the W / C ratio of the concrete. Be careful, with poorly made concrete, with high porosity, significant carbonation depths (30 to 40 mm) are observed.

- Propagation phase

In unreinforced concrete, carbonation has no negative influence on durability. On the contrary, the formation of insoluble $CaCO_3$ causes the porosity to decrease. For reinforced concrete, carbonation can be harmful by lowering the pH. In fact, the alkaline substances gradually disappear and the steel is no longer protected. It is said that he is no longer passivated. The question then is whether the steel will corrode and, if so, how quickly. Steel can only corrode if it is simultaneously put in the presence of water and oxygen. The corrosion reaction consists of the formation of an electrochemical cell along a rebar. On the anode side, the iron dissolves according to the following reaction:

$$\mathrm{Fe} \longrightarrow Fe^{2+} + 2e^{2-}$$

The electrons thus released are consumed at the cathode by the reduction of oxygen:

$$H_2\mathrm{O} + 1/2O_2 + 2e^{-} \longrightarrow 2\mathrm{H}O^{-}$$

$$Fe^{2+} + 2\mathrm{H}O^{-} \longrightarrow \mathrm{Fe}(OH)_2$$

$$\mathrm{Fe}(OH)_2 + O_2 \longrightarrow \text{rouille}$$

Corrosion by chloride diffusion

Chloride ions carried by water can be present in concrete: they can be present in concrete components (aggregates, etc.), be incorporated during mixing (chlorine setting accelerators, etc.) or even penetrate by diffusion or migrate by capillarity inside the concrete under concentration gradient from the external environment (sea water, de-icing salts, etc.). When the chloride content reaches or exceeds a critical value, it is said that there is depassivation of the protective layer of steel, the coating can no longer protect the reinforcements and corrosion begins if the quantities of water and oxygen are sufficient.

When the concrete structure is subjected to drying humidification cycles in the presence of chlorides, the latter can migrate with the liquid phase by convection, and as soon as the front of carbonation or penetration of chloride ions has passed through the "concrete of coating "and reaches the first reinforcement bed and rust begins, the depassivation takes place when the chloride content in the reinforcements exceeds a certain threshold (this threshold corresponds to a content of 0.4% relative to the mass cement). Corrosion is formed at the expense of the original metal. This phenomenon leads to both a significant increase in volume as well as a loss of the cross section of the reinforcement [21]. The reactions take place as follows:

$$Fe^{2+} + Cl^{-} \longrightarrow \mathrm{Fe}(Cl)_2$$

$$\mathrm{Fe}(Cl)_2 + 2(OH)^{-} \longrightarrow \mathrm{Fe}(OH)_2 + 2Cl^{-}$$

$$\mathrm{Fe}(OH)_2 + O_2 \longrightarrow \text{Rust}$$

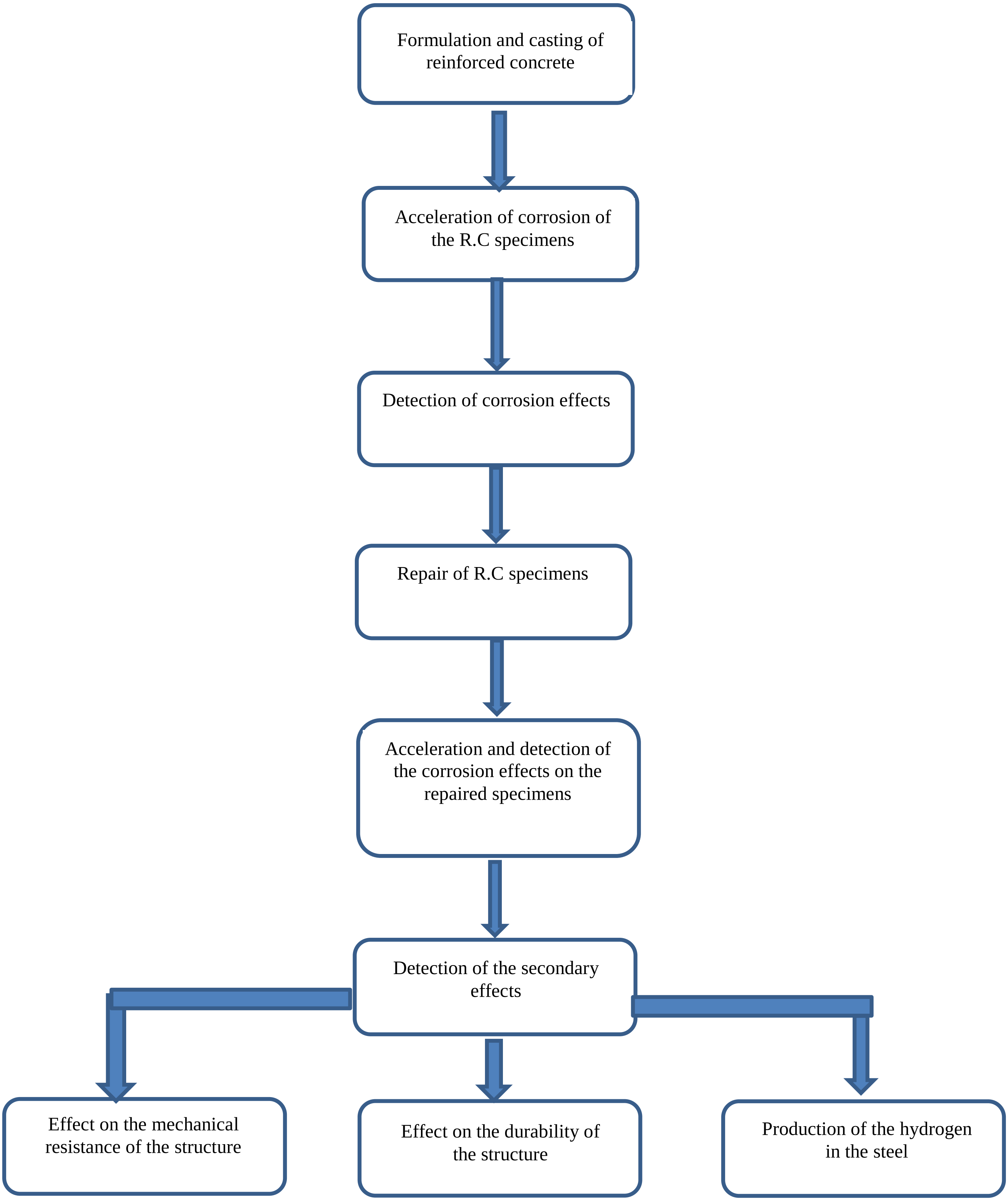
Rust is dangerous because it leads to a local reduction in the reinforcement section. When it gets too small, it will suddenly break, which can have dire consequences.

• *Alkali-reaction:*

The alkali reaction is a chemical reaction between silicas and silicates contained in potentially reactive aggregates (coming from cement, additions, additives, ...), and the alkalis of concrete in the presence of moisture. It corresponds to an attack of the aggregate by the basic medium of the concrete and causes the formation of a reaction gel (alkaline silicate), whose expansion generates, swellings. The disorders observable on the structures correspond to phenomena of crazing, major cracking, burst cones. These disorders can be associated with exudations of gel through the cracks created. In the case of aggregates with rapid reaction kinetics and high alkali contents, they can appear much earlier (less than 5 years). Finally, from a mechanical point of view, the tensile strength by bending or pure tension is more affected than the compressive strength and the modulus of elasticity can undergo significant decreases even before significant expansions are observed .It is recognized that there are three types of alkali reactions: alkali-silica reaction (the most common), alkali-silicate reaction, alkali-carbonate reaction [22].

2. Materials and methods

The diagram below shows the general approach that we will follow during our experiment. Each step will be detailed later to clarify the experiment procedure.



2.1 Formulation and casting of concrete specimens

Cylindrical geometry concrete specimens of dimension 15 * 30cm will be made. A 10 mm diameter steel bar is inserted into the concrete.

In our case we are going to formulate the concrete using the Dreux Gorisse method of class similar to the concrete used in port structures since these structures are the most affected by Chloride corrosion brought by salty sea water.

After formwork removal, the test pieces will be kept in a room at 100% relative humidity for 28 days before the application of the current.

The mortar test pieces are made up of aggregates of different granular classes, namely: sand 0/5, G1 4/10 and G2 10/20 and cement of type CLC (A) 45 PM with Dairy conforming to EN 197-1 [23] and Class 42.5 MPa ash. The water / cement ratio (W / C) equal to 0.35.

These test pieces will be subjected to slump tests during the preparation and crushing tests at 28 days

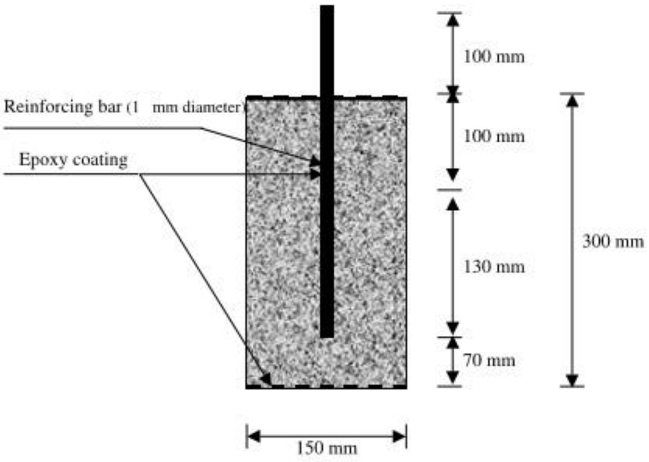


Figure 1: R.C Spécimen

2.2 Acceleration of corrosion

This experiment will be performed using the accelerated current corrosion test [24]. The configuration for the accelerated corrosion test is shown in the figure below. It includes a DC power supply, two stainless steel plates, a data logger, a test sample and the container with the required dosage of NaCl solution. The steel bar (anode / working electrode) of the sample is connected to the positive terminal and the stainless-steel plates (cathode / counter electrode) are connected to the negative terminal of the DC power source. The cathode will generate in the steel bars, which will promote the migration of chloride ions from the solution to the area adjacent to the metal, where accelerated oxidation reactions have occurred due to loss of electrons. In this experiment, we will also determine the tension and the duration sufficient to allow the evaluation of the loss of weight and thickness in the metal bars.

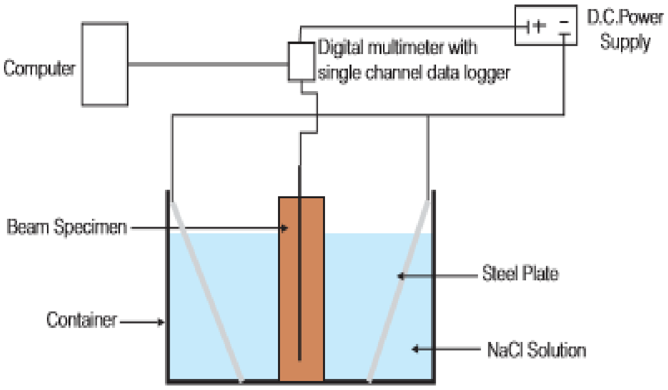


Figure 2: Corrosion Acceleration

The corrosion process is initiated by applying constant voltage to the system. The current response is continuously monitored and recorded by the data logger. In addition, the samples are inspected daily visually for cracks. The data logger is set to a suitable sampling frequency to record the corrosion current of the circuit. The accelerated corrosion test ends after cracking of the test piece when the rate of increase in corrosion current over time was negligible.

The figures below show the samples after application of the imposed current acceleration test

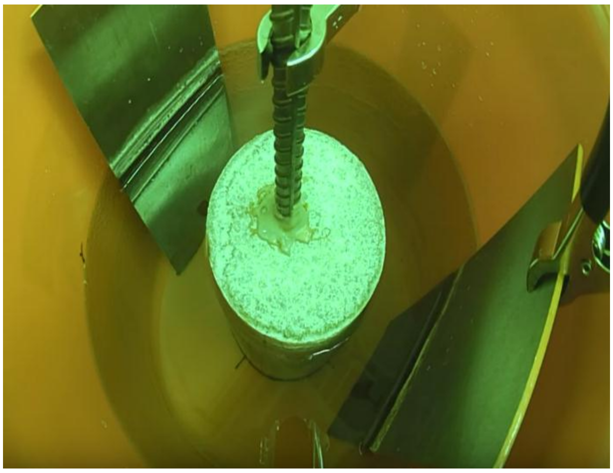


Figure 3: Before the application of the electric current

Figure 4: After the application of the electric current

2.3 *Detection of corrosion effects*

- ✓ **The LPR Method (LINEAR POLARIZATION RESISTANCE)**

This Method allows us to determine the corrosion rate by measuring the Icorr corrosion current in a simple, fast and non-destructive way [25.26]. The principle of LPR is based on the introduction of a small disturbing electrical signal ΔI, relative to a reference half-cell, to a steel bar corrodible using a surface counter electrode. The resulting potential change, ΔE is measured after an appropriate time for the balance to be restored. This technique is based on the calculation of the anode and cathode slopes of a polarization curve around its electrode potential. We first calculate Icorr according to the following equation:

$$I_{Cor} = {}^{B}/_{R_P}$$

- B a constant which varies from 13 to 52 mV depending on the state of the reinforcement in the concrete. This constant depends on the coefficients of anode Tafel βa and cathode βc.
- R_p The polarization resistance

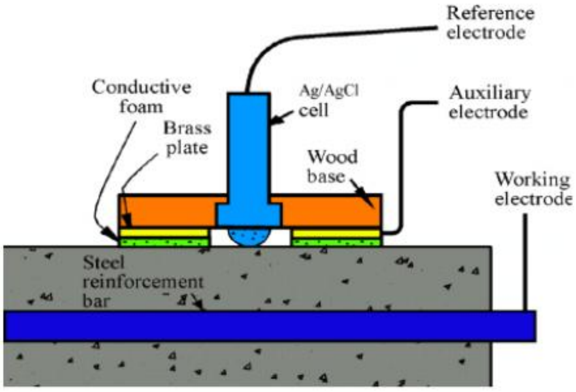
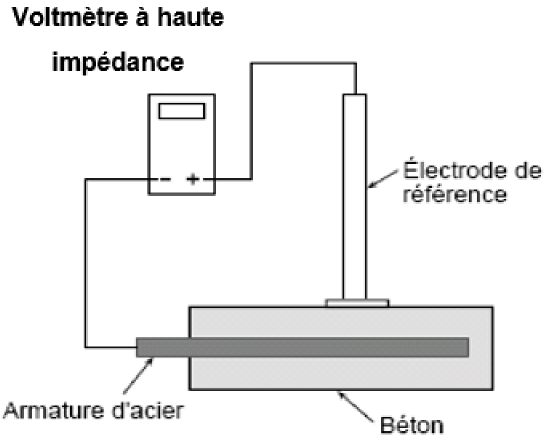


Figure 5: Measurement Using LPR

✓ Half Cell Potential

The aim of this method is to measure, using a high impedance voltmeter, the potential difference between the concrete reinforcement and a reference electrode (in general Cu / CuSO4) placed on the concrete facing [27]. The electrical conductivity is ensured by wetting the surface of the facing. The values of the free potentials measured on the structure were then compared with the values cited in standard ASTM C-876-91. They thus made it possible to estimate, under normal conditions of exposure of the concrete, the degree of possible rusting of the steels

Potentiel de corrosion mV vs Cu-CuSO$_4$	**Probabilité de corrosion**
> -200	Faible (< 10%)
-200 à -350	Incertaine (50%)
<-350	Elevée (90%)



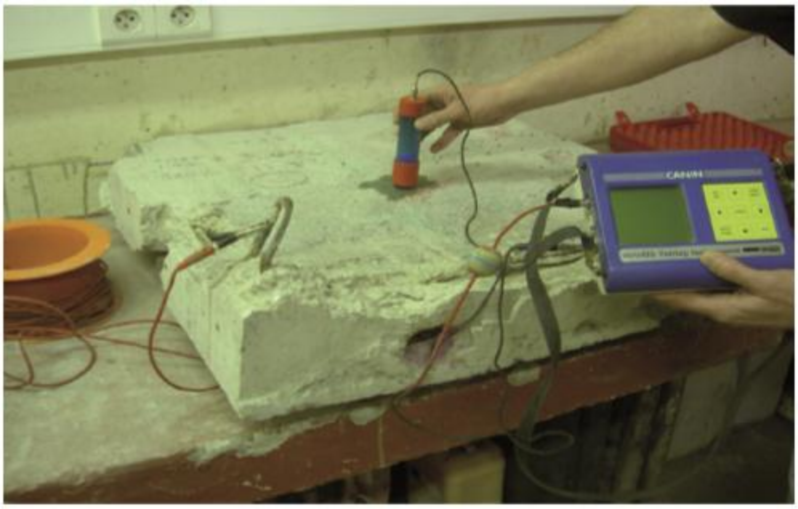


Figure 6: Measurement using the half-cell potential in CEREMA Lab

2.4 <u>Repair of the Reinforced concrete specimens</u>

The test consists in injecting a direct electric current, of the order of 1 to 5 A / m² of steel to be protected between the steel (cathode) and a Titan mesh placed on the surface of the coating concrete. This current causes the negatively charged chlorine ions to move towards the outside anode. When the chlorine ions reach the surface of the concrete, they pass into the electrolyte and can therefore be permanently removed from the concrete. This technique, unlike cathodic protection, is temporary with an application period of 4 to 5 weeks.

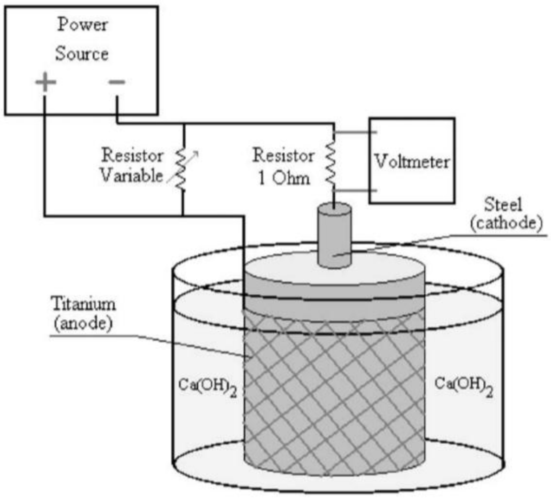


Figure 7: Repair of the specimen with the chloride extraction

2.5 <u>Detecting the side effects of these methods</u>

Despite the positive effects of electrochemical methods on the structure. However, Negative effects may appear when applying one of these techniques. These effects are generally due to the density, potential and current levels used which can influence the initial characteristics of the concrete. Indeed, the polarization of steel can generate a redistribution of ionic materials around steel. The latter phenomenon can cause negative effects such as damage to the steel-concrete interface, weakening of steels by hydrogen. And the dissolution of some of the concrete phases following the high pH value. In addition, the buildup of cations around the steel could start or accelerate the alkali-silica reaction [28-30].

✓ Hydrogen production on steel

The high polarization of steel, in the case of electrochemical extraction, causes the release of hydrogen on the surface of the steel [31-34]. However, the production of hydrogen causes a local increase in pressure which could induce cracks in the In addition, the adsorption of hydrogen by steel leads to embrittlement by hydrogen. To avoid this phenomenon it is necessary to make sure that the current carried out is lower than 1A / m², then the production of Hydrogen has no harmful effect on the whole of the structure

✓ Effects on the durability of the structure

For the sustainability part we will focus more specifically on the effects of these techniques on the alkali aggregate phenomenon. In fact, after treatment, the steels will be negatively charged because of the protective current, which can result in the creation of hydroxyl ions in the presence of water. These will be neutralized by the cations Na + and K + producing NaOH and KOH [35]. The presence of these alkalis can favour an initiation or one of RAG in the presence of reactive aggregates. To check the effect of these methods on the durability of concrete, we use MEB to check the presence of substances likely to initiate or accelerate the RAG in particular the silico-alkaline gel [36-39]. In our study, we did not observe the SEM or the presence of silica-alkaline gel.

✓ Effects on the mechanical resistance of the structure

In order to check if the application of these methods to change the mechanical resistance of the structure, it suffices to check its resistance by the 3-point bending test and check it with the 3-point bending tests for uncorroded test pieces.

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