Corrosion of reinforced concrete

I- Introduction

During its lifetime, the metallic structure of a building is attacked by the environment, especially by CO_2. Indeed, the iron is stable in basic media inside the concrete (pH = 12-14), but carbonates, dissolved in water, migrate through the concrete to the metallic part. This phenomenon implies a decrease of the pH localized around the metallic structure. This pH shift is represented by an arrow in the Pourbaix diagram [1] in Fig. 1. Then, at this acidic pH, the iron is no longer in its passive form but in its corrosive form. Consequently, the strength of the building is affected. For instance, the "Tour Perret" in Grenoble (Fig. 2), which is the first edifice built in reinforced concrete in Europe in 1924, is currently falling apart because of this process.
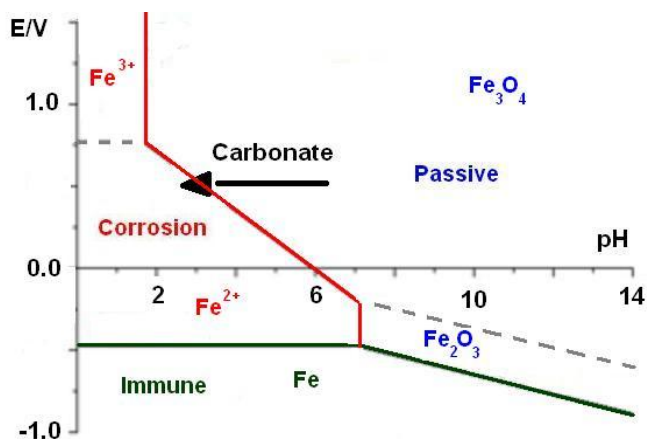
Fig. 2: The first edifice in reinforced concrete: the "Tour Perret" in Grenoble.

Fig. 1: Pourbaix diagram of iron [1].

In this context, an electrochemical process was developed to keep the neighborhood of the metallic rod in reinforced concrete in basic conditions [2-7]. For that, the materials to treat, which is a cathode, is immersed into a basic electrolytic paste (K_2CO_3 or Na_2CO_3) with an anode inserted in this paste (Fig. 3). The reduction of the water carried out at the metallic rod makes the media around the metallic rod more basic by production of OH^- (Eq. 1).
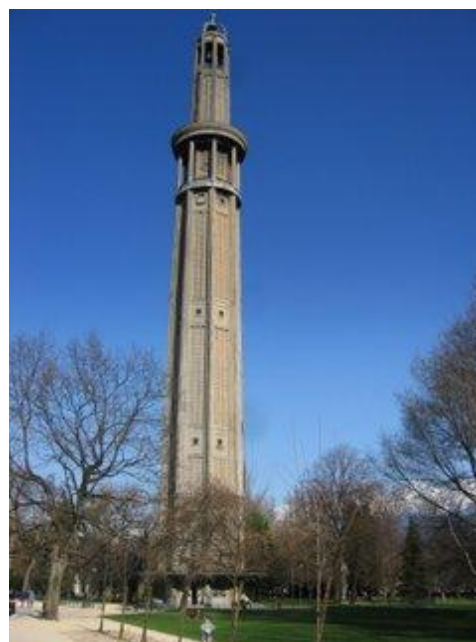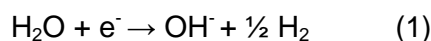
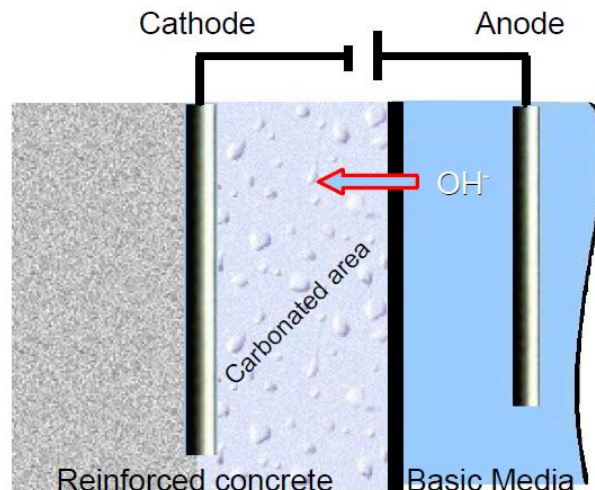$$H_2O + e^- \rightarrow OH^- + \tfrac{1}{2} H_2 \qquad (1)$$

Fig. 3: Scheme of realkalisation method.

In this note, the corrosion process of the metallic rod in a concrete block is investigated. Realkalisation (electroysis in basic media) is performed, and the benefits of the treatment are checked by Cyclic Potentiodynamic Polarization (CPP).

Bio-Logic Science Instruments, 1 rue de l'Europe, F-38640 Claix - tel: +33 476 98 68 31 – Fax: +33 476 98 69 09
Web: www.bio-logic.info

1

II-Experimental conditions

Investigations are carried out with the VMP3 instrument driven by EC-Lab® software in NaCl (3%) or NaOH solution (0.4 mol.L^{-1}). The concrete block is immersed for two days into the solution before measurements.

A three-electrode set-up is used:

- steel rod inside the concrete block as a working electrode with a surface area: $A = 10$ cm^2 (Fig. 4),
- Ag/AgCl electrode as reference electrode,
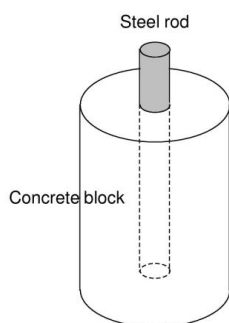- alloy wire as the counter electrode.

Fig. 4: Scheme of concrete reinforced block.

III- Results

III-1 Calculation of polarization resistance

First of all, we have to check if the material is under Tafel conditions [8,9]. For that, the resistance polarization (R_p) should be much higher than ohmic resistance (R_Ω). These two characteristics can be determined by electrochemical impedance spectroscopy (EIS) measurement (Fig. 5). The $R_\Omega = 202$ Ω is negligible versus $R_p > 12,800$ Ω (Fig. 6). Consequently, the conditions of « Tafel Fit » are respected.

R_p determination is also possible from voltamperometric measurements under a steady-state condition (very slow scan rate, *i.e.* 2.5 mV.min^{-1}) and in a narrow potential range (± 10 mV around the Open Circuit Voltage, *i.e.* -547 mV *vs.* Ag/AgCl). The voltamperogramm and the « R_p Fit » are displayed in Fig. 7 and give $R_p = 11,744$ Ω.

The R_p values determined by both methods are in agreement with each other.

It is possible to load the settings and the data files as PEIS_concrete_in_NaCl.mpr and MP_concrete_in_NaCl.mpr in the EC-Lab® Samples folder.

Fig. 5: "Parameters Settings" window of potentiostatic electrochemical impedance spectroscopy measurements (PEIS) performed in NaCl (3%).

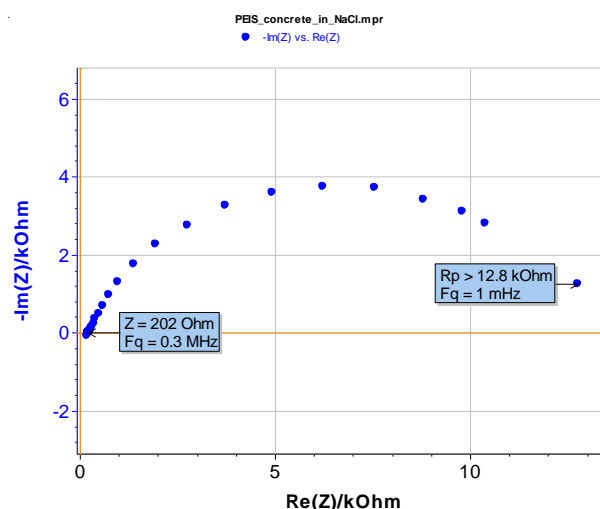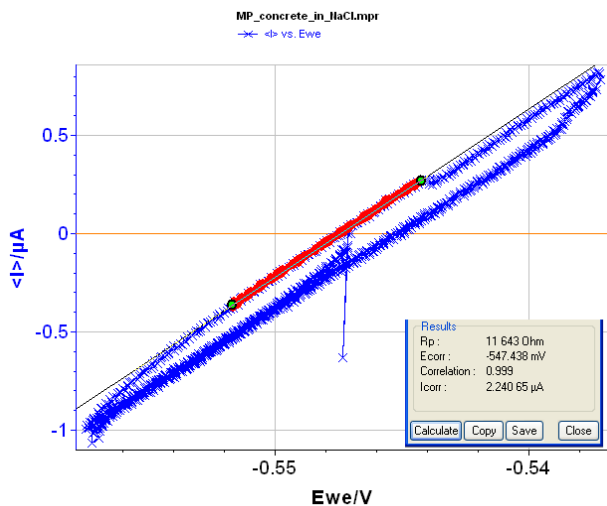**Fig. 6: Nyquist diagram of concrete block.**

Bio-Logic Science Instruments, 1 rue de l'Europe, F-38640 Claix - tel: +33 476 98 68 31 – Fax: +33 476 98 69 09
Web: www.bio-logic.info

2

Fig. 7: Voltamperogramm and "R$_p$ Fit"of the block in NaCl (3%).

III-2 Realkalisation

Realkalisation treatment is performed with the chronopotentiometric (CP) techniques in NaOH (0.4 mol.L^{-1}; pH = 13) for 66 h (Fig. 8) at I_s = -10 mA. Potential and charge during the electrolysis are plotted in Fig. 9. At the end of the electrolysis, a stable potential of -2.4 V *vs.* Ag/AgCl is reached.

III-3-Characterizations of the metallic rod.

In order to check the efficiency of the realkalisation, CPP experiments are carried out before and after the treatment. The parameters of these experiments are given in Fig. 10.
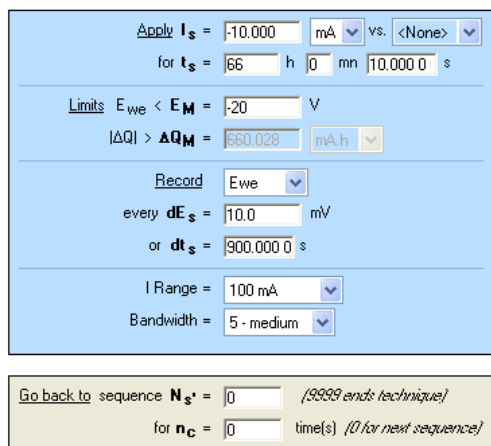

Fig. 8: "Parameters Settings" Window of chronopotentiometry (CP).
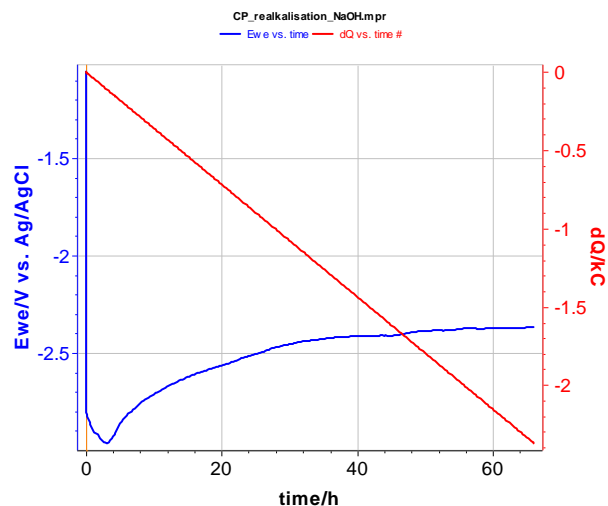

Fig. 9: Plot of potential (blue curve) and charge (red curve) during the electrolysis .

It is possible to load the settings and the data files as CP_Realkalisation_NaOH.mpr in the EC-Lab® Samples folder.

A comparison between CPP before and after realkalisation (Fig. 11) displays a cathodic shift due to steel rod reduction. "Tafel Fit" analysis is performed for both curves and gives E_{corr} = -616 and -1077 mV *vs.* Ag/AgCl for the CPP measurement performed before and after treatment, respectively.

Other parameters (I_{corr}, β_c, β_a, and corrosion rate) are computed (Fig. 11 and Table 1). The corrosion rate is given by Eq. 2:

$$CR = I_{corr}\, K\, EW\, /\, (d\, A) \qquad (2)$$

in which K is a constant, EW is the equivalent weight, d is the density, and A is the surface area of the electrode. In the case of steel, EW and d are 18.616 g/eq. and 7.8, respectively.

These fits show that corrosion rate is 50% higher before than after realkalisation. This decrease of the corrosion rate demonstrates the efficiency of the realkalisation process.

Bio-Logic Science Instruments, 1 rue de l'Europe, F-38640 Claix - tel: +33 476 98 68 31 – Fax: +33 476 98 69 09
Web: www.bio-logic.info

3

Fig. 10: "Parameters Settings" Window of CPP experiments.

It is possible to load the settings and the data files as CPP_Before_Realkalisation.mpr and CPP_After_Realkalisation.mpr in the EC-Lab® Samples folder.

Table 1: Data from CPP investigations.

	Before	**After**
E_{corr}/mV *vs.* Ag/AgCl	-616	-1097
I_{corr}/µA	404	272
β_c/mV *vs.* Ag/AgCl	646	240
β_a/mV *vs.* Ag/AgCl	670	325
Corrosion rate/mmpy*	0.315	0.213

*mmpy: mm per year

IV- Conclusion

This note demonstrates that electrochemical techniques are able to recondition (electrolysis) and characterize (CPP, impedance, and their corresponding analysis) the metallic structure of buildings.

It is an example of the contribution of the electrochemistry to the field of civil engineering.
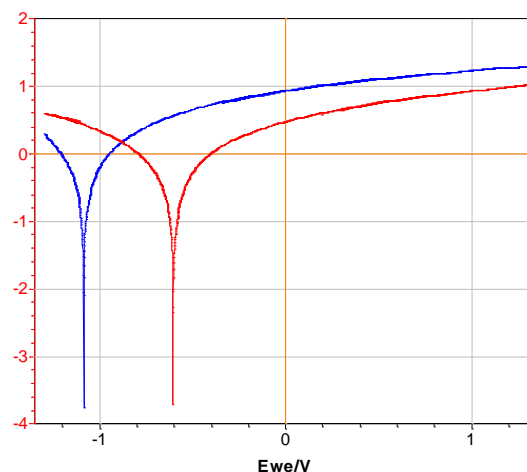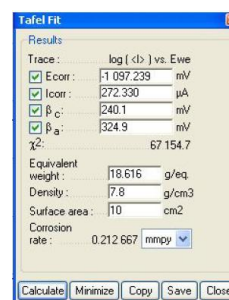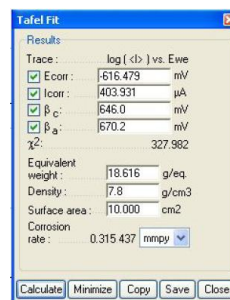

Before   After

Fig. 11: Evans diagram of the reinforced concrete before (in red) and after (in blue) realkalisation (top) and "Tafel Fit" results (bottom).

References

[1] Atlas d'équilibre électrochimiques, M. Pourbaix, ed. Gauthier-Villars (Paris) 1963.

[2] E. Cailleux, E. Marie-Victoire, L'actualité chimique, 2007, n°312-313, 22-28.

[3] http://www.novbeton.com/html/index-5.html

[4] N. Davison, G. Glass, A. Roberts, Transportation Research Board, 87th Annual Meeting, 2008.

[5] D. A. Koleva, K. van Breugel, J. H. W. de Wit, E. van Westing, N. Boshkov, A. L. A. Fraaij, J. Electrochem. Soc. 2007, 154(3), E45-E56.

[6] D. A. Koleva, J. H. W. de Wit, K. van Breugel, Z. F. Lodhi, E. van Westing, J. Electrochem. Soc. 2007, 154(4), P52-P61.

[7] D. A. Koleva, J. H. W. de Wit, K. van Breugel, Z. F. Lodhi, G. Ye, J. Electrochem. Soc. 2007, 154(5), C261-C271.

[8] M. Stern, A. L. Geary, J. Electrochem. Soc. 1957, 104(1), 56-63.

[9] Traité des Matériaux, Vol. 12, Corrosion et chimie de surfaces des métaux, D. Landolt, ed. Presses Polytechniques et Universitaires Romandes (Lausanne) 2003.

Bio-Logic Science Instruments, 1 rue de l'Europe, F-38640 Claix - tel: +33 476 98 68 31 – Fax: +33 476 98 69 09
Web: www.bio-logic.info

4