Desempeño de sonda basada en electrodo de referencia de cobre sulfato de cobre en sistema de monitoreo de corrosión in situ desarrollado para estructuras de concreto reforzado

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Abstract

This paper shows the performance of a probe based on a reference electrode of copper/copper sulfate in the development of an equipment of corrosion monitoring in situ for reinforced concrete structures subjected to carbonation. Designing electrochemical half-cell was performed with different reference electrodes using in this case a Copper / Copper Sulfate electrode (Cu-$CuSO_4$), and a steel rod (same material of the structure) to take as a variable the voltage generated by the system. The Voltages were evaluated following the standard ASTM C 876 - 91, which data are sampled, stored and transmitted to a web server using the developed equipment.

Keywords: corrosion monitoring in situ, half-cell potential, Embedded sensors, rebar corrosion, Carbonation**.**

Introduction

On rebars, major electrochemical reactions occur in the limited volume of aqueous solution in the pores of the concrete surrounding the metal. As a result of this process, the steel loses mass and its cross section decreases. However, this is not one of the evident risks related with rebars on concrete, instead, it is about of the solid products of corrosion. These are deposited in the close gap between concrete and steel; for being in a very small place, this process creates stresses that can break the concrete layer producing a progressive deterioration (1, 2, 3).

Normally, concrete is an excellent protection for the rebar inner the structure, but the exposition to different environmental conditions across its service life can accelerate the destructive process. Two of the better known causes of steel corrosion are the carbonation and chloride attack. Some factors rule the chlorides diffusion phenomena on concrete, such as type of cementitious material, water/binder relation, curing time, period of exposition to chlorides and other physical factors (4, 5, 6, 7).
Carbonation is one of the most important causes of structural deterioration on reinforced concrete in places with high levels of carbon dioxide (CO_2) as urban centers and parking lots

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located in buildings (8, 9). Given the degree of pollution in capital cities and its higher levels of CO_2, can be expected that some concrete structures present advanced carbonation degrees. In pathology studies of buildings and bridges in capital cities, it has been found that certain elements show signs of deterioration owing to steel corrosion, attributable to carbonation and (in some elements, this phenomena has made progress more than expected) (1, 10, 11, 12, 13).

This work presents the performance evaluation of a design of an electrochemical half-cell based on a Copper / Copper Sulfate reference electrode (*Cu-CuSO*$_4$), and a steel rod of the evaluated structure, implemented on the development of an equipment to perform the in situ corrosion monitoring of reinforced concrete subjected to carbonation.

Methodology

General Design

The system designed allows the user to command the start of data sampling via a text message using the general packet radio service (GPRS). The microcontroller through its wireless transmission equipment, evaluates the signal that has come via the text message and starts the test. Then the microcontroller stores all measurements obtained during the test, once completed, the microcontroller sends the data packets (which has been previously stored in memory) to its GSM / GPRS module, which transmits to the Web server where the variables are stored in its own database, that enables the customer to visualize through a web application, the measured potential as graphs, corresponding to the level of corrosion of reinforced concrete structure (figure 1).

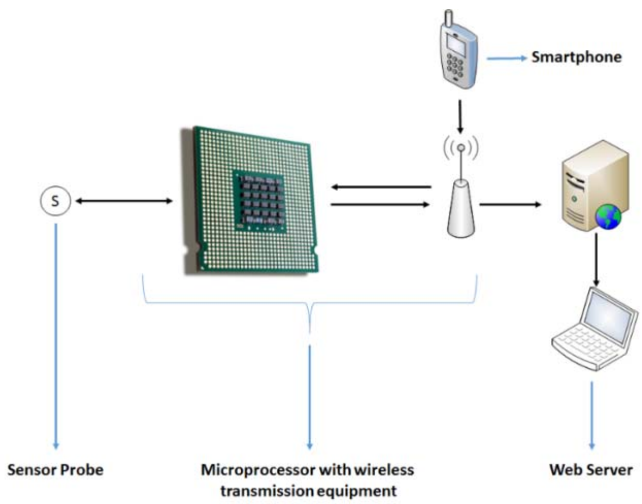


Figure 1 - a) Design Scheme

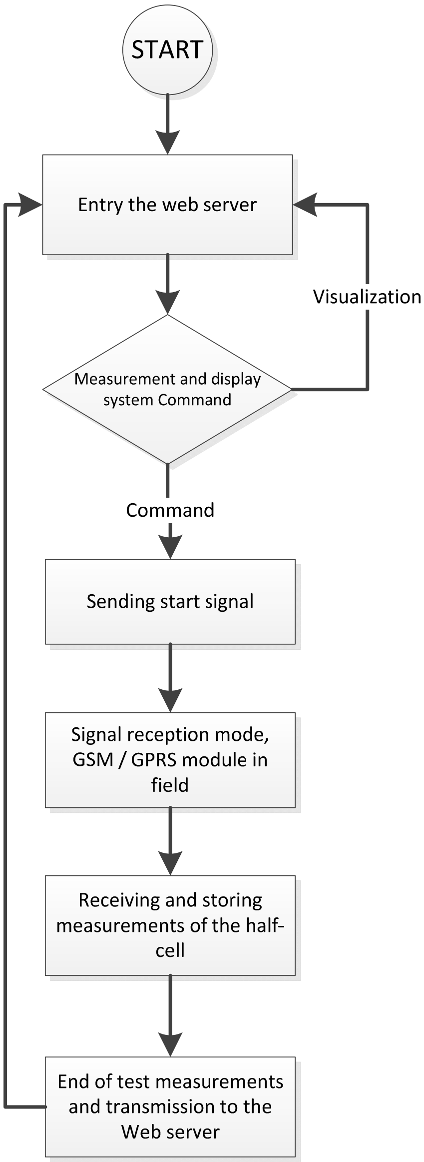


Figure 1 - b) Flowchart of operational design

Design of embeddable half-cell

The reinforcement steels are typically protected by the alkaline nature of concrete. If that alkalinity is compromised at some point, the corrosion in the steel will initiate if oxygen and moisture combine. The corrosion reaction will promote the anodic and cathodic activity across the rebar, thus generating a corrosion cell by the electric difference between the two mentioned regions.

The half-cell potential measurements are a virtually non-destructive technique, simple and low cost, that allow to estimate the corrosion risk of rebar on concrete (14). This method uses a voltmeter for measuring the electric potential difference (ΔV) between the steel and half-cell. The analysis of the electric potential can indicate whether corrosion is taking place in the rebar or not (Figure 2).

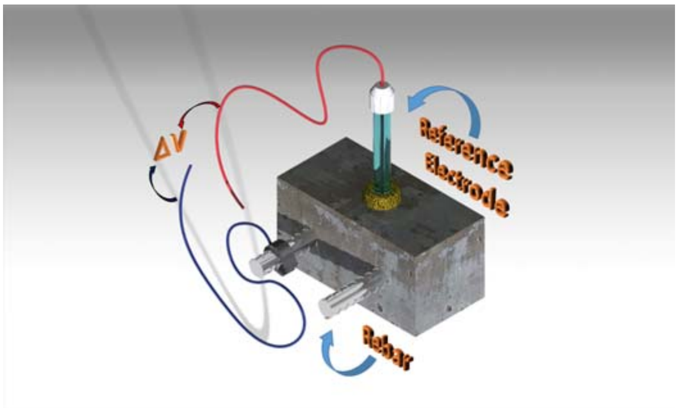


Figure 2 - Disposition of electrochemical half-cell as standard ASTM C876-91 (14)

As figure 2 shows, it is necessary to remove the rust from steel and then, connect it to the common port of the voltmeter while the reference electrode is connected to the positive terminal; this setting allows to obtain the voltage and determining the corrosive state of the structure.

In order to take the measurements through an embeddable element, it was proposed the construction of an electrochemical half-cell which can be inserted into the concrete indefinitely, and that provides the measurement voltage corresponding to the corrosive state. To this purpose, it was used a reference electrode based on Copper/Copper Sulfate (*Cu-$CuSO_4$*) and structural steel segments of 25 centimeters length. With the reference electrode and each steel segment (connected to a copper wire of diameter 3mm, isolating contact with silicone), a probe coated with mortar was made (Figure 3). The bare copper wire was taken to the device using a shielded cable and a 3-pin XLR connector, which allows to isolate the signal from outer and stabilize the subsequent reading.

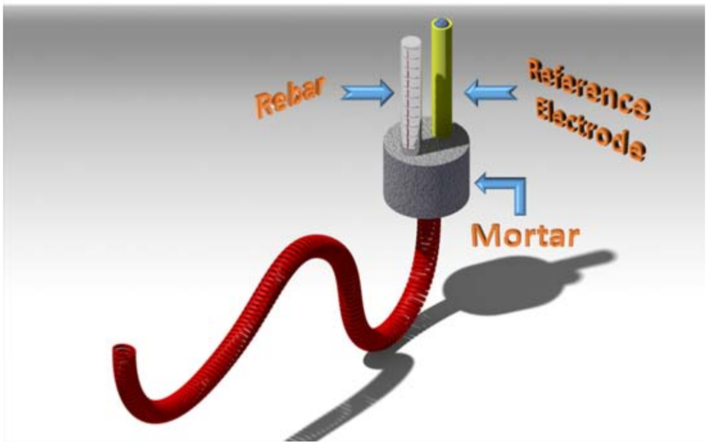


Figure 3 - Probe coated with mortar

The probes were finally embedded in reinforced concrete according to manufacturer's specifications, locating the probe at a drilling depth of 4 inches (Figure 4).

Prior to installation, the reference electrode was pre-soak in a clean bucket of fresh potable water from 20 to 30 seconds, then after placing the electrode into the hole, the remaining water was poured over the electrode. This procedure is important because it creates a condition for the surrounding soil/concrete and backfill to penetrate and lock into the pores of the electrode reference cell.

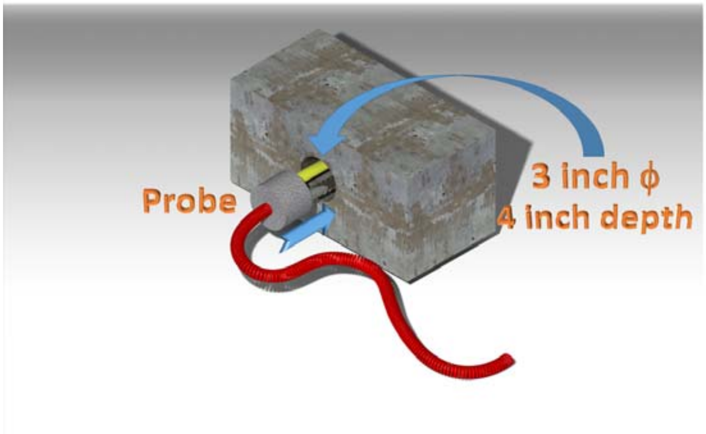


Figure 4 - Probe inserted in reinforced concrete section

Design of the data acquisition system

The data acquisition system was designed based on previous developments on Arduino technology, where was used the Wireless SD shield (Figure 5) in order to use the slot for memory cards MicroSD. The design allows to storage a reading of the half-cell voltage every second in memory, it is not necessary to obtain higher rates of data acquisition in such measures as the voltage during the data collection process does not vary considerably. Each package measurement data is stored in a *.txt* file.

The storage process acquires approximately 15 minutes of data, allowing to take 900 readings. This process is led by the user, who must give the order by sending a text message with the word START addressed to the mobile phonenumber assigned to the corresponding measurement system.

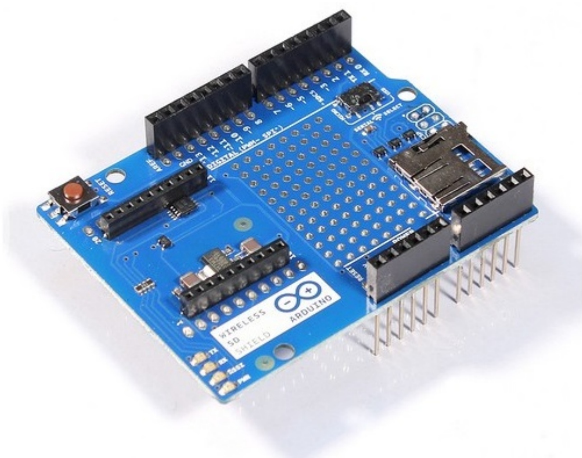


Figure 5 - Shield MicroSD Arduino (15)

Design of Data Transmission System

In order to make available to the user in any location, the information obtained in the stage of storing, GSM / GPRS technology was adapted by the shield for Arduino GSM / GPRS M95 (Figure 6). The module provides the possibility to use the cellular network by inserting a subscriber identity module Card (SIM Card) which assigns the system a single telephone number capable of handle receiving text messages which command the acquisition stage data.

Once the system has acquired and stored the package of 900 measurements during 15 minutes in the *.txt* file, using the FTP protocol (File Transfer Protocol), through AT commands, instructs the embedded M95 for sending the file to the web server, which receives all data in a *php* database.

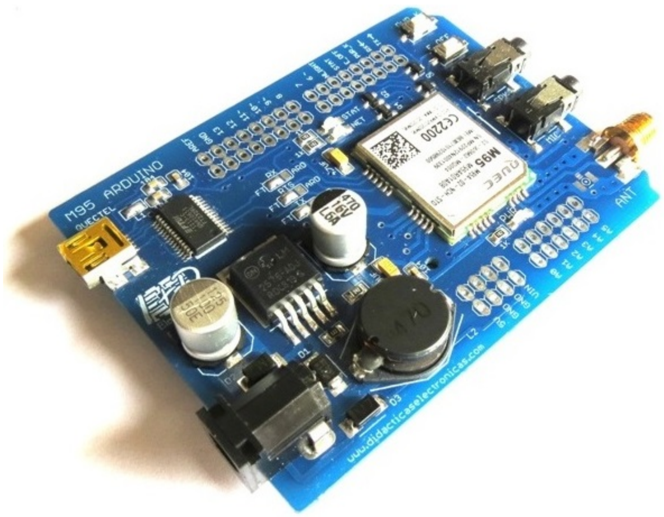


Figure 6 - Shield M95 Arduino (15)

Web supervisory design

The web supervisory of the corrosive state of rebar inner the concrete structure its located in a web server based on *php* code, which through the jpgraph plugin allows to extract data stored in the *php* database and give them a format to present the data graphically to the user.

The supervisory differentiates the 3 regions of corrosion probability of ASTM C876-91 according to the range of the measured voltage (table 1) by segmenting the graphical canvas in 3 parts each identified by a label. The tendency voltage data obtained is plotted from the database on the segmentation (Figure 7).

Table 1 – Corrosion probability VS half-cell potential (14)

Measured Voltage (Volts)	Corrosion probability
Voltage > -0.20	10% or less
-0.20 > Voltage > -0.35	region of uncertainty
Voltage < -0.35	90% or greater

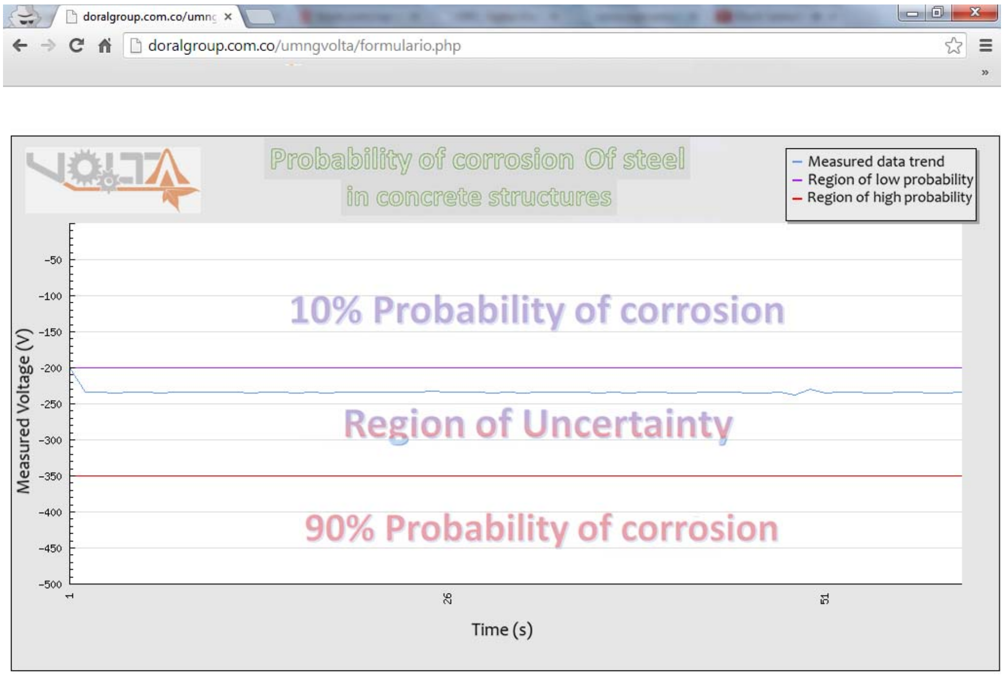


Figure 7 – Web supervisory

Starting up the system with Cu/CuSO₄ reference electrode as half-cell

It were prepared cylindrical specimens of portland concrete with a diameter of 50mm and 100mm length. A portion of the specimen was subjected to an environment in a climatic chamber with a CO_2 concentration of 4%, a relative moisture of 65% and a temperature of 25°C, within which the entry of CO_2 occurred by the exposed faces. The remaining portion was subjected to environmental conditions where CO_2 concentrations corresponds to 0.003%.

On each specimen, the installation of the half-cell probe based on *Cu/CuSO*$_4$ was performed to a depth of 4 inches from the surface. The reference electrode was tested by the manufacturer against a calomel cell at 25°C to obtain a voltage of +64 mV and +60 mV variance from standard +4 mV.

Additionally, each specimen was provided with an independent electrode of the same compound, and the reinforcement was exposed in order to reproduce the conventional ASTM C876-91 technique.

Results and discussion

It was performed the simultaneous monitoring of the corrosion potential using two sets of measurements over an interval of time of 2600 hours (Figures 8, 9), during this interval the voltage measurements were obtained for the samples in the environments free of carbon dioxide and saturated subjected to 4% (Table 2, 3).

Table 2 – Measurements on concrete specimens subjected to environmental condition (CO_2 concentration of 0.003%)

Exposure time (h)	Corrosion potential with designed half-cell based on *Cu-CuSO₄* (mV)	Corrosion potential with standard method ASTM C876-91 (mV)
0	-154	-168
350	-126	-128
700	-16	-13
1050	117.6	124.9
1700	-213	-204
2600	-291	-283

a) b)

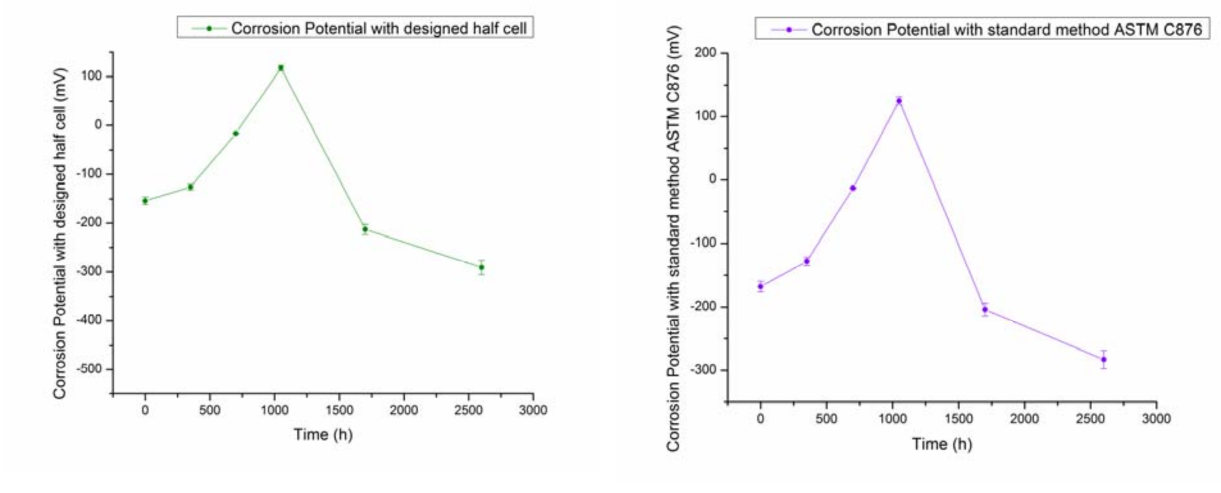
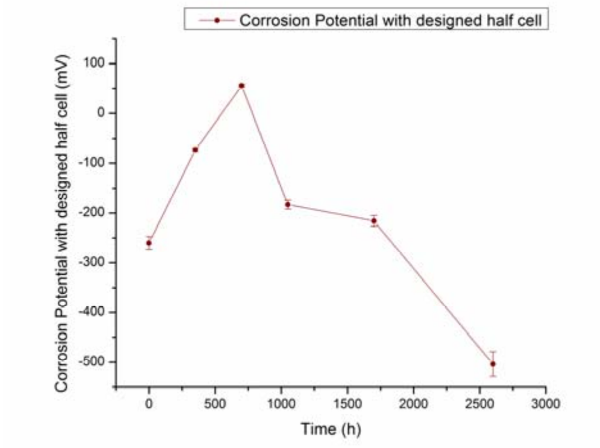


Figure 8 – Corrosion potential measure on environmental conditions using a) Designed half-cell based on *Cu-CuSO₄*, b) Standard method ASTM C876

Table 3 – Measurements on concrete specimens subjected to conditions of saturation of 4% CO_2

Exposure time (h)	Corrosion potential with designed half-cell based on *Cu-CuSO$_4$* (mV)	Corrosion potential with standard method ASTM C876-91 (mV)
0	-260	-231
350	-73	-67
700	55.6	57.8
1050	-183	-177
1700	-216	-221
2600	-504	-517

a)



b)

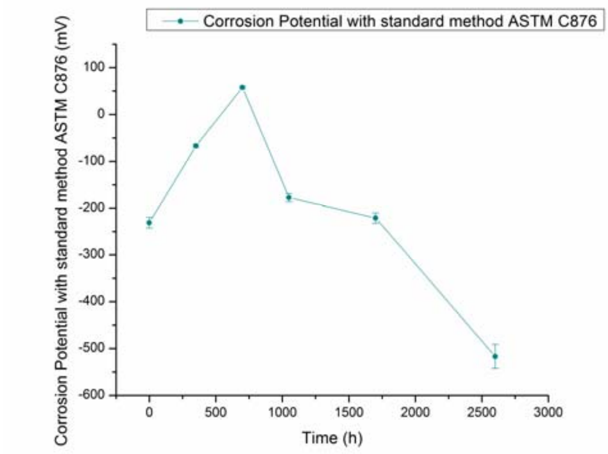


Figure 9 – Corrosion potential measure on conditions with CO_2 using a) Designed half-cell based on *Cu-CuSO$_4$*, b) Standard method ASTM C876

Once those measurements were obtained, they were compared in order to determine the error percentage using the developed probe versus the measures of ASTM standard (Figure 10 and 11), to determine the performance of the probe design (Table 4 and 5)

Table 4 – Error on measurements using the developed probe based on *Cu-CuSO4* compared with ASTM standard (specimens under ambient conditions)

Exposure time (h)	Error (%)
0	8.33%
350	1.56%
700	23.08%
1050	5.84%
1700	4.41%
2600	2.83%

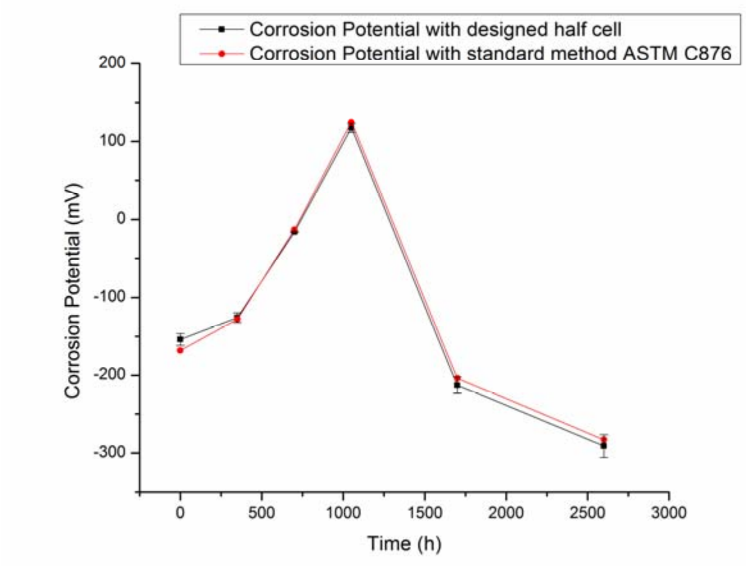


Figure 10 – Corrosion potential measure on environmental conditions

Table 5 – Error on measurements using the developed probe based on *Cu-CuSO4* compared with ASTM standard (specimens subjected to saturated conditions with CO_2)

Exposure time (h)	Error (%)
0	12.55%
350	8.96%
700	3.81%
1050	3.39%
1700	2.26%
2600	2.51%

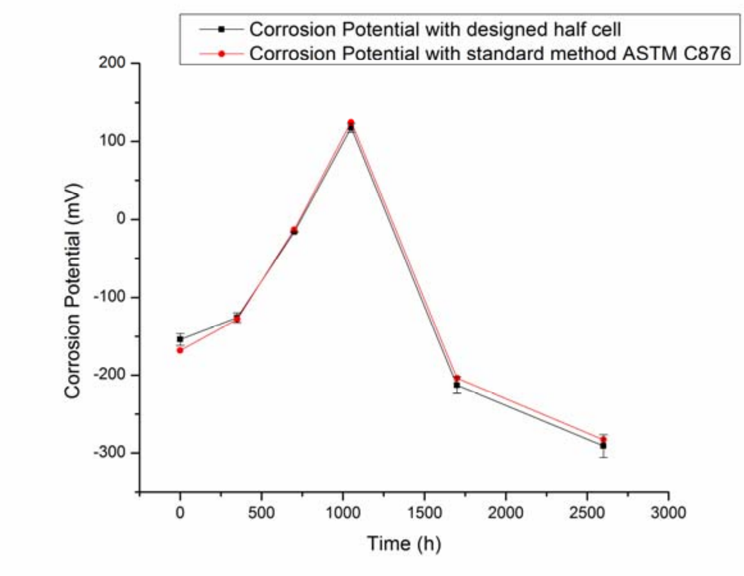


Figure 11 – Corrosion potential measure on conditions with CO_2

In the measurements obtained in the two environments to which were subjected the specimens and the two measurement systems, is evidenced a maximum error of 23% at 700 hours in environmental conditions and a minimum error of 1.56% at 350 hours on the same ambient conditions, obtaining an average error across all measurements in the two test of the 6.62%

Conclusions

Through this study, the viability of the designed probe based on a reference electrode of *Cu-CuSO$_4$* and a steel rod was verified in terms of their performance on the developed equipment of corrosion monitoring in situ for reinforced concrete structures subjected to carbonation, finding a mean error of 6.62% (compared to standard method ASTM C876-91) over the entire voltage measurements, registered during 2600 hours in specimens subjected to an environment free of carbon dioxide and an environment with a concentrated 4% saturation thereof.

Using data obtained from the designed probe, compared to the standard method ASTM C876-91 and the average error of voltage measurements, it is possible to diagnose and classify concrete in the 3 regions of probability of corrosion of rebar, both free environments and under the influence of carbon dioxide.

The probe designed in this paper, is only applicable for environments exposed to the influence of carbon dioxide or free from this. If faced with a corrosive environment with a different factor, such as chlorides in marine environments, it is necessary to change the reference electrode to a material that gives better performance against this variable, as is the case with silver / chloride silver (Ag-AgCl). This exchange is necessary, since the presence of chloride causes a change in the negative direction in the reference potential in pair copper / copper sulfate (16).

Bibliographical references

(1) APERADOR, W., MEJÍA DE GUTIÉRREZ, R., BASTIDAS, D. M. Steel corrosion behavior in carbonated alkali-activated slag concrete. **Corrosion Science**, v. 51, n. 9, p. 2027-2033, Sep. 2009.
(2) ROA-RODRIGUEZ, G., APERADOR, W., DELGADO, A. Calculation of Chloride Penetration Profile in Concrete Structures. **International Journal of Electrochemical Science**. v. 8, p. 5022-5035, Apr. 2013.
(3) GASTALDI, M., BERTOLINI, L. Effect of temperature on the corrosion behaviour of low-nickel duplex stainless steel bars in concrete. **Cement and Concrete Research**. V. 56, p. 52-60
(4) RAUPACH, M., SCHIESSL, P. Monitoring system for the penetration of chlorides, carbonation and the corrosion risk for the reinforcement. **Construction and Building Materials**. V. 11, n. 4, p. 207-214.
(5) TAE, SUNG-HO. Corrosion inhibition of steel in concrete with natural inorganic minerals in corrosive environments due to chloride attack. **Construction and Building Materials**. V.35, p. 270-280, 2012.
(6) MORENO, M., MORRIS, W., ALVAREZ, M. G., DUFFÓ, G. S. Corrosion of reinforcing steel in simulated concrete pore solutions: Effect of carbonation and chloride content. **Corrosion Science**. V. 46, n. 11, p. 2681-2699, 2004.
(7) RAUPACH, M., SCHIESSL, P. Monitoring system for the penetration of chlorides, carbonation and the corrosion risk for the reinforcement. **Construction and Building Materials**. V. 11, n. 4, p. 207-214.
(8) ROY, S. K., NORTHWOOD, D. O., POH, K. B. Effect of plastering on the carbonation of a 19-year-old reinforced concrete building. **Construction and Building Materials**. V. 10, n. 4, p. 267-272.
(9) SAETTA, A. V., VITALIANI R. V. Experimental investigation and numerical modeling of carbonation process in reinforced concrete structures: Part I: Theoretical formulation. **Cement and Concrete Research**. V. 34, n. 4, p. 571-579.
(10) APERADOR, W., DELGADO, A., VERA, E. Monitoreo mediante EIS del acero embebido en un concreto de escoria activada alcalinamente expuesto a carbonatación. **Revista ingeniería de construcción**. v. 26, n. 1, p. 81-94, Apr. 2011.
(11) ROA-RODRIGUEZ, G., APERADOR, W., VERA, E. Software para el cálculo de la velocidad de deterioro de los hormigones sometidos a carbonatación. **Revista Latinoamericana de Metalurgia y Materiales**. V. 34, n. 1, p. 45-54, 2014.
(12) FARAHI, E., PURNELL, P., SHORT, N. R. Supercritical carbonation of calcareous composites: Influence of mix design. **Cement and Concrete Composites**. V. 43, p. 12-19.
(13) HUANG, N. M., CHANG J. J., LIANG M. T. Effect of plastering on the carbonation of a 35-year-old reinforced concrete building. **Construction and Building Materials**. V. 29, p. 206-214.
(14) ASTM Standard C876-09, 1991, Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete. **ASTM International**, West Conshohocken, PA, 2003, DOI: 10.1520/C0876-09.
(15) Arduino. Retrieved February 12, 2014, from *http://www.arduino.cc/*
(16) ANSUINI, F. J., DIMOND, J. R., Factors Affecting the Accuracy of Reference Electrodes. **Materials Performance**. V. 33, n. 11, p. 14-17, Nov. 1994.