Monitoring of Concrete Permeability, Carbonation and Corrosion Rates in the Concrete of the Containers of El Cabril (Spain) Disposal

C. Andrade1, J.L. Sagrera1†, I. Martínez1, M. García2 and P. Zuloaga3
1Institute of Construction Science “Eduardo Torroja”, CSIC, Madrid, Spain
2Geotecnia y Cimientos S.A. (Geocisa), Madrid, Spain
3Enresa, Madrid, Spain

ABSTRACT

Aging of concrete in nuclear repositories is an important problem due to this material is a part of the engineering barrier for long term storage of nuclear wastes. In order to study the real on-site aging of concrete, Enresa has undertaken a monitoring program in collaboration with IETcc and Geocisa. Among the several parameters that characterize concrete aging, those selected for being controlled in the real containers of the disposal of El Cabril (Spain) have been: air permeability, carbonation, resistivity, corrosion potential and corrosion rate. These parameters are measured twice per year in the real size containers, except the carbonation, that being a destructive measurement is measured in specimens stored in the same climatic conditions. The analysis of these results in combination with the numerous other studies carried out in samples at laboratory level, enables to confirm that were correct the assumptions made in the service life model taken for the concrete in the design phase of the installation.

Keywords: Aging, concrete, polarisation resistance, corrosion rate, air permeability, carbonation.

INTRODUCTION

Corrosion of reinforcement is one of the main durability problems of concrete structures. The corrosion is induced by two main factors: the carbonation of the concrete cover and the penetration of chlorides providing from marine atmosphere or from chemicals in contact with concrete. Carbonation generally aims into uniform corrosion of the steel bar while chlorides mainly induce localised corrosion. Both types of corrosion are of electrochemical nature. There is a third type of corrosion named stress corrosion cracking, SCC, whose mechanism is not entirely electrochemical, but the mechanical stress co-operates for its development. This last type will not be considered in present paper.

Reinforcement corrosion is not a common problem in nuclear power plants due to the limited life of these installations, except in case of cooling towers where frequent corrosion problems have been noticed. It can be however a key aspect to be taken into account when dealing with extension of power plant service life. It is as well a very relevant aspect in long term storage or repository disposals where lives beyond 300 years are usually targeted. In order to study the real on-site aging of concrete, Enresa has undertaken a monitoring program in collaboration with IETcc and Geocisa. On this program, air permeability, carbonation, resistivity, corrosion potential and corrosion rate have been studied in the concrete of the real containers of the disposal of El Cabril (Spain).

ON-SITE TECHNIQUES FOR CORROSION MEASUREMENT

Corrosion Potential and resistivity maps.

Up to the present the main techniques used on-site for appraising corrosion of reinforcements are of electrochemical nature due to that is the basis of the corrosion process. Because of its simplicity, the measurement of Ecorr (rest or corrosion potential) is the method most frequently used in field determinations. From these measurements, potential maps are drawn which reveal those zones that are most likely to undergo corrosion in the active state1. However, such measurements have only a qualitative character, which may make data difficult to be interpreted2. This is due the potential only informs on the risk of corrosion and not in its actual activity. In addition, the developing of macrocells may as well mislead the deductions because corroding zones polarize the surrounding areas, which may seem corroding as well, when they are cathodic areas of the macrocell. In spite of which potential mapping still has a function to accomplish as a qualitative indication of the general performance and a complement of the other on-site techniques.

The same that said for the potential can be stated on Resistivity, ρ, measurements3, which sometimes are used jointly with Ec Orr mapping. The ρ values indicate the degree of moisture content of the concrete, which is related to the corrosion rate when the steel is actively corroding, but which may mislead the interpretation in passive conditions. On Figure 1 is represented a risk map of a slab. The risk level has been calculated by a combination of these two parameters: Ec Orr and ρ.
Polarization Resistance

Laboratory measurements

The only electrochemical technique with quantitative ability regarding the corrosion rate is the so-called Polarization Resistance, $R_p^4$. This technique has been extensively used in the laboratory. It is based on the application of a small electrical perturbation to the metal by means of a counter and a reference electrode. Providing the electrical signal is uniformly distributed throughout the reinforcement, the $\Delta E/\Delta I$ ratio defines $R_p$. The corrosion current, $I_{corr}$, is inversely proportional to $R_p$, $I_{corr} = B/R_p$ where $B$ is a constant. $R_p$ can be measured by means of D.C. or A.C. techniques$^5$, both of which have specific features in order to obtain a reliable corrosion current value in agreement with gravimetric losses.

On site measurements

Direct estimation of True $R_p$ values from $\Delta E/\Delta I$ measurements is usually unfeasible in large real concrete structures. This is because the applied electric signal tends to vanish with distance from the counter electrode, CE rather than spread uniformly across the working electrode, WE. Therefore, the polarization by the electric signal is not uniform, and it reaches a certain distance that is named the critical length, $L_{crit}$. Hence, $\Delta E/\Delta I$ measurements on large structures using a small counter electrode provides an apparent polarization resistance ($R_p^{app}$) that differs from the true $R_p$ value depending on the experimental conditions$^6$. Thus, if the metal is actively corroding, the current applied from a small CE located on the concrete surface is 'drained' very efficiently by the metal and it tends to confine itself on a small surface area. Conversely, if the metal is passive and $R_p$ is high, the current applied tends to spread far away (e.g., around 50 cm) from the application point. Therefore, the apparent $R_p$ approaches the true $R_p$ for actively corroding reinforcement, but when the steel is passive, the large distance reached by the current needs a quantitative treatment.

Modulated confinement of the current (guard ring) method.

There are several ways of accounting for a True $R_p$ value, among which the most extended one is the use of a guard ring$^7$, in order to confine the current in a particular rebar area, as Figure 2 depicts. The measurement is made by applying a galvanostatic step, lasting 30-100 seconds, from the central counter. Then, another counter current is applied from the external ring, and this external current is modulated by means of the two reference electrodes called “ring controllers” in order to equilibrate internal and external currents, which enables a correct confinement, and therefore, calculation of $R_p$. By means of this electrical delimitation to a small zone of the polarized area, any localised spot or pit can be first, localised, and second its measurement can be made by minimising the inherent error of $R_p$. Not all guarded techniques are efficient. Only that using a “Modulated Confinement” controlled by two small sensors for the guard ring control placed between the central auxiliary electrode and the ring, shown in Figure 2, is able to efficiently confine the current within a predetermined area. The use of guard rings without this control leads into too high values of the $I_{corr}$ for moderate and low values, and the error introduced in the case of very localised pits, is very high.
Figure 2. Modulated confinement of the current (guard ring) method

RANGES OF CORROSION RATE VALUES MEASURED ON-SITE

The experience on real structures\textsuperscript{7, 8} has confirmed the ranges of values previously recorded in laboratory experiments\textsuperscript{4}.

<table>
<thead>
<tr>
<th>Corrosion Rate Range</th>
<th>Risk Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤0.2 (\mu\text{A/cm}^2)</td>
<td>Negligible</td>
</tr>
<tr>
<td>0.2 (\mu\text{A/cm}^2) &lt; (I_{corr}) &lt; 0.5 (\mu\text{A/cm}^2)</td>
<td>Low</td>
</tr>
<tr>
<td>0.5 (\mu\text{A/cm}^2) &lt; (I_{corr}) &lt; 1 (\mu\text{A/cm}^2)</td>
<td>Moderate</td>
</tr>
<tr>
<td>&gt;1 (\mu\text{A/cm}^2)</td>
<td>High</td>
</tr>
</tbody>
</table>

Table-1. Ranges of corrosion rate and risk levels.

In general, values of corrosion rates higher than 1\(\mu\text{A/cm}^2\) are seldom measured while values between 0.1-1\(\mu\text{A/cm}^2\) are the most frequent. When the steel is passive very low values (smaller than 0.05-0.1\(\mu\text{A/cm}^2\)) are recorded.

A comparison of on-site \(I_{corr}\) values to electrical resistivity has allowed the authors to also rank the resistivity ones.

MEASUREMENT OF CONCRETE CARBONATION

Carbonation occurs in concrete because the material has an alkaline nature and the calcium bearing phases present are attacked by carbon dioxide of the air and converted to calcium carbonate. In addition, cement paste contains 25-50 wt% calcium hydroxide (\(\text{Ca(OH)}_2\)), which means that the pH of the pore solution is at least 12.5. The pH of a fully carbonated paste is about 7-8.

If CO2 from air or from water penetrates, the concrete will carbonate according to:

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}
\]

The carbonation process requires the presence of a certain amount of water. If the concrete is too dry (RH <40%) CO2 cannot dissolve and no carbonation occurs. If on the other hand it is too wet (RH >90%) CO2 cannot enter the concrete and the concrete will not carbonate. Optimal conditions for carbonation occur at a RH of 50% (range 40-90%).

Normal carbonation results in a decrease of the porosity making the carbonated paste stronger. Carbonation is therefore an advantage in non-reinforced concrete. However, it is a disadvantage in reinforced concrete, as pH of carbonated concrete drops to about 7; a value below the passivation threshold of steel.

The advance of carbonated front through the concrete cover can be determined by using a pH indicator (Phenolftaleine). On this way, it’s possible to determine the carbonation velocity \((V_{\text{CO2}})\) of a concrete in different environments, making different measurements with time. The expression used in present study for the determination of the \(V_{\text{CO2}}\) is the well known:

\[
X = V_{\text{CO2}} t^{0.5}
\]  \hspace{1cm} [1]

Were \(X\) is the depth of the carbonated front at each time \((t)\).

AIR PERMEABILITY MEASUREMENTS IN CONCRETE

Air permeability is considered a rough estimation of concrete compactness. In present study is measured by a non-destructive method. There is a non-destructive test for “in situ” measurement of the permeability to air of a concrete
coating. The system is based in creating a vacuum inside a cell placed on its surface, and to measure how long does it take for the pressure to be back to the atmospheric value. The main aspects of the method are: a cell with an inward chamber and a regulator to keep the pressure in balance inside this central chamber (measurement) and in the surrounding chamber (preservation ring). This ensures a single air flow direction towards the central chamber, avoiding a spurious transversal flow. The data of the measurement are processed by a microprocessor that indicates the permeability coefficient value at the end of the test which last 2 to 12 minutes.

The quality of the cover is determined depending on the permeability coefficient value. Experimental tests using this method lets to make a classification of the concrete cover on five different classes. On this classification, Class 1 correspond to high resistance concretes (> 60 Mpa), well compacted and cured, and Class 5 correspond to low resistance concretes (> 15Mpa), bad cured.

<table>
<thead>
<tr>
<th>Quality of concrete cover</th>
<th>Class</th>
<th>KT (10^{-16} \text{ m}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very Poor</td>
<td>5</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Poor</td>
<td>4</td>
<td>1 - 10</td>
</tr>
<tr>
<td>Normal</td>
<td>3</td>
<td>0.1 - 1</td>
</tr>
<tr>
<td>Good</td>
<td>2</td>
<td>0.01 - 0.1</td>
</tr>
<tr>
<td>Very Good</td>
<td>1</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Table-2. Quality concrete cover classification.

RESULTS

Electrochemical measurements

Resistivity, corrosion potential and corrosion rate of reinforcement are the electrochemical parameters measured in the concrete cells in El Cabril – Cordoba – Spain. These three parameters are measured twice a year with the corrosion rate meter Gecor 6. Figure 3 shows the results of resistivity measured during several years. Concrete resistivity has shown values between 100 and 300 KΩ.cm, these values indicates that concrete is dry. More than 90% of the corrosion potential values are more positive than –200 mV (using Cu/CuSO4 as reference electrode), (Figure 4) indicating a non-active corrosion. The corrosion rate values (Figure 5) are below the depassivation limit (0.1 µA/cm²), so they indicate the passivity of reinforcement, as expected.

RESISTIVITY, WALLS A, B, C AND D

Figure 3. Results of resistivity measured during several years over the internal walls of the real container.
Figure 4. Results of corrosion potential measured during several years over the internal walls of the real container.

Air permeability measurements

These measurements have been made directly over the concrete surface in the same points than the corrosion measurements. The trend shows that the coefficient KT changes between $10^{-2}$ and $10^1 \times 10^{-6}$ m$^2$ (Figure 6). These values provide a concrete class between 1 and 3, following the Torrent’s classification, which is shown on Figure 7. That means a normal, good or very good quality of the concrete cover.

There is not a criteria for the relation between resitivity and permeability, but as is mentioned by Torrent, when the concrete is not completely dry, it’s necessary to calibrate the classification with the resistivity values, as is presented on Figure 8. Making the classification on this way, results observed are the same than on Figure 7.
Figure 6. Results of permeability coefficient (KT) measured during several years over the internal walls of the real concrete container.

Figure 7. Concrete class following the quality of the cover. Variation with time on different points of the container.

Figure 8. Relationship between resistivity and KT. Nomogram for the quality cover classification.

Carbonation measurements

Because of the destructive character of the technique used for carbonation measurements, the study of carbonation penetration on the container concrete has been made by the exposure of cylindrical control specimens on two different environments (outside and inside). The specimens were cured under water and exposed until today to El Cabril atmosphere and to the interior of a building. Some of them have been buried.
Results on specimens exposed during 10,3 years are given each year, two specimens on each exposure are broken and carbonation is observed applying phenolftaleine on spray. On the central part of each specimen, two slices are prepared (Figure 10). These slices are cut on two equal pieces, leaving two rectangular surfaces which dimensions are 3 x 15 cm, that are impregnated with the indicator. The non-carbonated part of the concrete surface presents a violet colour, while the non-carbonated one doesn’t present any particular coloration, as is shown on Figure 9. On this figure is observed how carbonation front is around 5 mm length.

**Figure 9. Specimen slices after phenolftalein application**

Carbonation coefficient it’s calculated using expression [1]. As can be observed on Figure 10, the change of this value with time seems to be stabilised after 7 years of exposure, presenting almost a constant value during the last three years. This fact confirms the good carbonation resistance on this concrete. It is important to notice that the specimens that were held in the interior of a building present a higher $V_{co2}$ than those exposed to the atmosphere. With $V_{co2}$ around 1 mm/year$^{0.5}$ means that the carbonation front will not reach the 40 mm cover thickness until 1600 years.

Finally, concerning the buried specimens they show any carbonation sign until present.

**Figure 10. Evolution with time of the carbonation coefficient calculated on the control specimens in El Cabril.**

**FINAL COMMENTS**

Corrosion of reinforcement can be approximately model and accurately measured on-site. The periodical corrosion rate measurements on its monitoring seems very necessary to assess present conditions of concrete structures and is a very useful tool in the case of cooling towers of power plants. Techniques based in the measurement of Polarization Resistance have been implemented in portable corrosion rate meters to obtain corrosion rate values, and corrosion-data-loggers are now operative in pilot containers to monitor corrosion related parameters.

The quality of concrete cover can be determined by a non-destructive technique measuring air permeability. This measurement together with to the carbonation velocity provides important information about the service life of the structure.
ACKNOWLEDGEMENTS

The authors thank to Enresa the funding provided to develop the research presented in the paper.

REFERENCES

2. Elsener, B and Bóhni, H. Corrosion Rates of Steel in Concrete, N.S. Berke, V.Chaker and D. Whiting (Eds.), ASTM STP 1065, pp. 143-156. (1990)