STUDIES CONCERNING THE REINFORCEMENT CORROSION OF CONCRETE VAULTS FOR INTERMEDIATE-LEVEL RADIOACTIVE WASTE

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Abstract
The Argentine Atomic Energy Commission (CNEA) is responsible for developing the nuclear waste disposal management programme. This programme contemplates the design and construction of a facility for the final disposal of intermediate-level radioactive wastes. The proposed model is a near-surface monolithic repository based on those in operation in L’Aube, France and El Cabril, Spain. The design of this type of repository is based on the use of multiple, independent and redundant barriers. Since the vault and cover are major components of the engineered barriers, the durability of these concrete structures is an important aspect for the facility integrity. This work presents a laboratory investigation performed on reinforced concrete specimens manufactured with a High Performance Concrete recently developed by the National Institute of Industrial Technology (Argentine), in order to predict the service life of the intermediate level radioactive waste disposal vaults from data obtained from electrochemical techniques. On the other hand, data obtained with corrosion sensors embedded in a vault prototype is also included. These sensors allow on-line measurements of several parameters related to the corrosion process such as rebar corrosion potential and corrosion current density; incoming oxygen flow that reaches the metal surface; concrete electrical resistivity; chloride concentration and internal concrete temperature. All the information obtained from both, laboratory tests and sensors will be used for the final design of the container in order to achieve a service life more or equal than the foreseen durability for this type of facilities.
1. INTRODUCTION

The National Atomic Energy Commission (CNEA) of the Argentine Republic is the implementing authority to perform all activities related to the radioactive waste management and sets up the Radioactive Waste Management National Program (PNGRR) [1]. In order to achieve its objectives the National Radioactive Waste Management Program is in charge of the adoption of the most appropriate technological solution for the management of such wastes and the scientific-technological support.

In this context, for the Intermediate Level Radioactive Waste (ILRW) a monolithic repository near surface based on those in operation in L’Aubé, France and El Cabril, Spain, is foreseen. The design concept of this type of repositories is the use of multiple, redundant and independent barriers. The model considers a 300 years post-closure institutional control. Wastes will be immobilized in cement matrices and packed in 200 litre drums or in special concrete containers. An sketch of the proposed model is shown in Figure 1.

![Figure 1. Sketch of the repository design.](image)

Intermediate level radioactive solid waste originated from operation and maintenance activities of the two Power Plants, consist mainly of mechanical filters from the primary circuit of the reactor and by spent ionic exchange resin beds. Such intermediate level radioactive solid waste is under interim storage at the facilities of each Power Plant awaiting treatment and conditioning but most of this waste will arise from the decommissioning of the nuclear power plants. Then, the start up of the intermediate level radioactive waste repository is linked to the decommissioning of the nuclear power plants and it should be operative approximately by the year 2023.

The barriers foreseen for the ILRW repository can be divided into two categories: physical and chemical barriers. The physical barriers are meant to avoid the intrusion of water, people and animals, and the release of radio nuclides. While the chemical barriers are intended to restrict radio nuclide migration by adsorption and ion-exchange once the soluble radio nuclides have been released from the source. The barriers which will be used in the near surface repository include: waste forms, metallic disposal containers, backfill and buffer materials, vaults and cover and geological media. The vault and cover are major components of the engineered barriers, and due to the fact that these barriers are made of reinforced concrete, their durability is an important aspect regarding the integrity of the facility. For those reasons a research programme on concrete durability was initiated several years ago.
The research and development are focussed to design a durable concrete and to establish the methodology to determine the longevity of concrete, through the knowledge of its performance in the long-term under disposal conditions. Of course, durability is influenced by the environment to which the concrete is exposed to, by the quality of the constituents and their proportion in the mix design and by structural designs and construction techniques, among other factors.

This work presents laboratory and field investigations performed on concrete specimens made with two different formulations. These specimens contain rebar segments and are exposed to different aggressive environments, in order to predict the service life of the ILRW concrete vaults from data obtained from electrochemical techniques. The diffusion coefficient of aggressive species, such as chloride and carbon dioxide, was also determined. In addition, a full scale concrete prototype was constructed and instrumented with sensors specially designed in order to monitor the evolution of the rebar corrosion rate in time.

2. EXPERIMENTAL TECHNIQUE

The study was performed using concrete specimens containing rebar segments. The specimens are 25 cm high and have a square section of 15 cm per side. Each specimen contained 3 rebar segments (DNA-420 type), two straight ones and one containing two welds. The rebars are 10 mm diameter and present an exposed area of 30 cm$^2$. The chemical composition of the reinforcing bars used in the study is as follows: C, 0.41%; Mn, 0.73%; Cu, 0.27%; Ni, 0.13%; Si, 0.28%; P, <0.01%; S, 0.02%; N, 0.008%, Fe, balance. At the concrete-air interface the rebars were isolated by epoxy resin in order to avoid crevice corrosion. The rebar segments were positioned in such a way that a 3 cm concrete cover was achieved. Each specimen contains an metal-metal oxide (MMO) internal reference electrode [2] with a diameter of 3 mm and 50 mm long, located in its centre.

Two different concretes were used in this study and those were selected based, among other properties, on the mechanical properties and workability. The composition of the concrete used as well as their compressive strength are summarized in Table 1.

Table 1: Composition and mechanical properties of the concretes used in the present work.

<table>
<thead>
<tr>
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<th>Base Concrete (BC)</th>
<th>Base concrete + Silica Fume (SF)</th>
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<tbody>
<tr>
<td>Water (kg/m$^3$)</td>
<td>154.1</td>
<td>158.6</td>
</tr>
<tr>
<td>Cement CAH40 (SR) IRAM 50000 (kg/m$^3$)</td>
<td>416.4</td>
<td>379.9</td>
</tr>
<tr>
<td>Silica Fume (kg/m$^3$)</td>
<td>---</td>
<td>42.2</td>
</tr>
<tr>
<td>Sand (kg/m$^3$)</td>
<td>813.4</td>
<td>837.4</td>
</tr>
<tr>
<td>Coarse Aggregate (kg/m$^3$)</td>
<td>995.2</td>
<td>1024.5</td>
</tr>
<tr>
<td>Additives (kg/m$^3$)</td>
<td>2.94</td>
<td>3.4</td>
</tr>
<tr>
<td>w/c</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td>Compressive strength (MPa) 28 days</td>
<td>53.6 ± 1.3</td>
<td>56.3 ± 2.2</td>
</tr>
<tr>
<td>Air Permeability (m$^2$)</td>
<td>0.018 x 10$^{-16}$</td>
<td>0.004 x 10$^{-16}$</td>
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A total of 18 specimens were made for each concrete. After a conditioning period of 100 days the specimens were exposed to three different conditions: immersed in a 3.5 % NaCl aqueous solution, immersed in a 5 % Na$_2$SO$_4$ aqueous solution and exposed to natural carbonation in the laboratory atmosphere (temperatures between 20° and 25°C, and 60-70% relative humidity).

The electrochemical parameters normally used to characterise the corrosion behaviour of reinforcing steel in concrete have been monitored periodically during approximately 850 days (about 2.3 years). These parameters include the corrosion potential ($E_{\text{corr}}$), the corrosion current density ($I_{\text{corr}}$) obtained from polarisation resistance ($R_p$) measurements and the electrical resistivity of concrete ($\rho$) determined from resistance measurements between the two straight rebar segments.

The $E_{\text{corr}}$ measurements were measured using a high input impedance multimeter connected to the IRE. These measurements were then corrected against a copper/saturated copper sulphate reference electrode (SCSE). The results were evaluated according ASTM standard C-876 [3]. $R_p$ was evaluated as $\Delta V/\Delta I$ [4] from potential sweep within $E_{\text{corr}} \pm 0.01$ V at a scan rate of $10^{-4}$ V.s$^{-1}$. The results were corrected to compensate the IR drop error. $R_p$ values were used to calculate the rebar corrosion current density ($I_{\text{corr}}$) according to the Stern-Geary relationship as follows: $I_{\text{corr}} = B/R_p$, where B values should take into account whether the steel segments are in the active or passive state. Andrade et al. [5] reported typical values for steel embedded in mortar: the value of B for steel in the passive state ($E_{\text{corr}} > -0.2$ V$_{\text{SCSE}}$) is 0.052 V, while for steel in the active state ($E_{\text{corr}} < -0.3$ V$_{\text{SCSE}}$) is 0.026 V.

The concrete electrical resistance ($R_c$) was measured between bars using an earth ohmmeter. These values were used to estimate the electrical resistivity of the concrete as $\rho = k R_s$, where $k$ is the geometric cell constant measured experimentally with solutions of known electrical resistivity.

The chloride transport parameters were obtained using cylindrical concrete specimens (10 cm diameters and 10 cm height) according to the AASHTO T259 Standard Method of Test for Resistance of Concrete to Chloride Ion Penetration [6]. In order to analyse the chloride transport mechanism in concrete, the Effective Diffusion Coefficient ($D_{\text{eff}}$) as well as the Chloride Surface Concentration ($C_s$) were determined by solving Fick’s second law. On the other hand, the carbonation depth was determined using the phenolphthalein test after a 1245 days exposure.

Finally, several corrosion sensors specially developed were embedded in a concrete wall built with BC (simulating a corner of the cells) in order to monitor the evolution along time of the temperature inside the structure, the corrosion potential and the corrosion current density of the reinforcing bars, the electrical resistivity of concrete, the availability of oxygen and the chloride ions concentration in concrete (Figure 2). This monitoring has been followed up for the last year, and it will be continued for the next years.

3. RESULTS AND DISCUSSION

Figure 3 show the evolution of the corrosion potentials of the reinforcing bars as a function of time (up to 820 days) for specimens made with BC. It can be seen that, for specimens exposed to laboratory environment, the corrosion potential is more positive than 0 V$_{\text{SCSE}}$ revealing a passive state of the steel. On the other hand, the rebar corrosion potential of specimens immersed in 3.5% NaCl aqueous solution shows a decrease immediately after
exposure, and reaches an almost constant value of -0.2 V$_{SCSE}$ after 500 days exposure. Finally, the rebar corrosion potential of specimens immersed in 5% Na$_2$SO$_4$ aqueous solution shows a similar behaviour to that observed on specimens immersed in the NaCl solution: a decrease after exposure and a final value of about -0.2 V$_{SCSE}$ after 820 days exposure. The results are similar to those obtained with base concrete + silica fume (SF).

Figure 2. Instrumented concrete wall simulating the corner of a cell.

Figure 3. Evolution of the corrosion potential as a function of time for steel bars embedded in BC and exposed to different environments.

The rebar corrosion current density ($i_{corr}$) of specimens made with BC and exposed to laboratory environment remained almost constant and close to $10^{-9}$ A/cm$^2$ during the 820 days of exposure (Figure 4). This results are a clear indication that steel presents a passive state.
On the other hand, the $i_{corr}$ of specimens immersed in 3.5% NaCl solution and 5% Na$_2$SO$_4$ solution show a value slightly higher ($3 \times 10^{-9}$ A/cm$^2$). Again, the results are similar to those measured in rebars embedded in SF concrete.

![Figure 4. Evolution of the corrosion current density as a function of time for steel bars embedded in BC and exposed to different environments.](image)

As for the effect of the use of pre-welded reinforcing bars on the value of $i_{corr}$ for specimens made with BC and exposed to laboratory environment and immersed in 3.5 NaCl solutions, it was found that while in the first case the presence of welds do not modify the value of the $i_{corr}$, in the last case, the $i_{corr}$ is three fold higher when the reinforcing bars are welded. This lead to the conclusion that the use of pre-welded reinforcing bars deserves a detailed study to ensure their durability.

The evolution of the electrical resistivity of BC ($\rho$) exposed to different conditions shows that for specimens exposed to laboratory environment the electrical resistivity increase with the exposure time, being this fact an indication of the continuous concrete hydration process. These specimens showed $\rho$ values of about 20 kOhm.cm after 820 days exposure.

On the other hand, the electrical resistivity of specimens immersed in NaCl and Na$_2$SO$_4$ solutions were very similar, showing values close to 2 kOhm.cm the same period of time. It is worth to mention that no appreciable differences where found in the $E_{corr}$, $i_{corr}$ and $\rho$ values when comparing the different types of concretes studied in the present work (BC and SF).

By applying the AASHTO T259 Standard and after measuring the total chloride concentration profiles after 10 month exposure, the values of the chloride effective diffusion coefficient ($D_{ef}$) and chloride surface concentration values ($C_s$) were calculated and are shown in Table 2. These values correlate well with those reported by Bamforth [7] for marine structures (extreme conditions).
Table 2: Effective Diffusion Coefficient ($D_{\text{eff}}$) and Chloride Surface Concentration ($C_s$) of the concretes studied in the present work.

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<th>Base concrete + Silica Fume (SF)</th>
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<tbody>
<tr>
<td>$D_{\text{eff}}$ ($m^2/s$)</td>
<td>$8.9 \times 10^{-11}$ ($\pm 1.7 \times 10^{-11}$)</td>
<td>$3.5 \times 10^{-12}$ ($\pm 0.8 \times 10^{-12}$)</td>
</tr>
<tr>
<td>$C_s$ (% concrete)</td>
<td>0.43 ($\pm 0.03$)</td>
<td>0.53 ($\pm 0.18$)</td>
</tr>
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</table>

For the Base Concrete, the maximum carbonation depth after 1250 days was 5.2 mm that gives a carbonation rate ($k$ in the equation $x = k \cdot t^{0.5}$, $x$ being the carbonation depth and $t$ the exposure time), of 2.82 mm.year$^{-0.5}$, value that is close to those reported by Andrade et al. for a concrete for similar purposes [8]. On the other hand, no evidence of carbonation was observed on the Base Concrete + Silica Fume specimens. Taking into account a detection limit of 1 mm, the constant $k$ is lower than 0.54 mm.year$^{-0.5}$.

Figure 5 shows, as an example, some parameters obtained with 2 sensors embedded in a prototype of a vault wall. The results obtained for the $E_{\text{corr}}$ are consistent with those obtained in laboratory (after a conversion from MMO electrode to SCSE), however, the $i_{\text{corr}}$ values are higher than those predicted by laboratory measurement, a fact that deserve further investigations.

![Figure 5. Evolution of some parameters measured with sensors embedded in a prototype of a vault wall built with BC.](image)

According to the threshold $E_{\text{corr}}$ and $i_{\text{corr}}$ values for the passive to active transition for steel corrosion in concrete ($E_{\text{corr}} < -0.35$ V$_{\text{SCSE}}$ and $i_{\text{corr}} > 0.1 \mu\text{A/cm}^2$), the results obtained in laboratory in all cases, show that the steel reinforcement remains in the passive state or close to the boundary between low corrosion risk and intermediate corrosion risk.

Based on the Tuutí´s service life model [9], no propagation period must be considered for this type of facilities because, according to the service criterion proposed by Andrade and Alonso [10] for reinforced concrete in ILRW facilities, it is assumed that the durability of
these structures ends once rebar corrosion has been initiated. In order to fulfil this criterion, the concrete must be designed to completely avoid corrosion during the period of almost 300 years (however, it should be mentioned that the effect of a passive state over 300 years deserves further study). If corrosion (propagation period) is likely to occur during the ILRW disposal service life, the theoretical safety is very much reduced and a high risk of losing the barrier characteristics exists before accomplishing the expected life. Two consequences of this statement are: ILRW facilities must not be located in places where chlorides, sulphates or the carbonation front could reach the rebar during the service life of the structure. In addition, all other degradation processes, which might affect cover integrity and impermeability (leaching, sulphate attack, freezing and thawing, etc), have to be avoided as part of the design phase.

Up to now, the site for the near surface disposal facility has not been determined yet. The location considered should be compatible with long-term concrete performance. That is to say, the site should be at a considerable distance from chloride containing environments (e.g. marine environments) and located in an area with no abnormal content of carbon dioxide and other acid contaminants. Then, the most important cause of reinforced corrosion is the carbonation during the period in which the vaults are kept in contact with air [9]. Knowing the diffusion rate of CO$_2$ in concrete, after 300 years, the carbonation depth would be about 45 mm for the Base Concrete and less than 9 mm for the Base Concrete + Silica Fume, that is to say, the containers should be designed taking into account this value. If it is so, it is expected that the concrete under study fulfil the requirements for the foreseen life-time. Besides, in the present work, the influence of both chloride and sulphate ions on the corrosion behaviour of rebars was studied taking into account the remote possibility of accidental contaminations.

**CONCLUSIONS**

- The concrete studied in the present work provides a passive status of corrosion to steel rebars characterised by corrosion rates lower than 0.1 $\mu$A/cm$^2$ ($< 1$ $\mu$m/year$^1$).
- The values for the chloride effective diffusion coefficient ($D_{eff}$) and its surface concentration when reinforced concrete is exposed to extreme conditions (in contact with sea water), are low enough and the carbonation ratio is also adequate to comply with the foreseen specifications.
- To guarantee a 300 year service life, the rebars corrosion rate of the ILRW disposal containers, must be lower than 0.01 $\mu$A/cm$^2$ ($< 0.1$ $\mu$m/year$^1$). the measured data show that this durability criterion is fulfilled.
- The electric resistivity of concrete has a tendency to increase with time, which reflects the continuous curing process showed by concrete at an early stage.
- In order to fully evaluate the behaviour of concrete durability from the rebar corrosion standpoint, after the selection of the site for the near surface disposal facility is made, the medium and long term evolution of the electrochemical parameters under study will be followed up.
ACKNOWLEDGEMENTS

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