# Durability of Concrete Vaults for Radioactive Waste Disposal

### by G.S. Duffó, E.A. Arva, S.B. Farina, C.M. Giordano, and C.J. Lafont

Synopsis: The development of a program for the design and construction of a facility for the final disposal of intermediate-level radioactive wastes in the Argentine Republic is responsibility of the Atomic Energy Commission (CNEA). The proposed model is the near-surface monolithic repository similar to that in operation in 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 made of reinforced concrete and they are major components of the engineered barriers, the durability of these concrete structures is an important aspect for the facilities' integrity. This work presents a laboratory and field investigation performed during the last 6 years on reinforced concrete specimens made with high-performance concrete, 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, the development of corrosion sensors that allow on-line measurements of reinforcing steel corrosion potential and corrosion current density, incoming oxygen flow that reaches the metal surface, concrete electrical resistivity, chloride concentration, and internal concrete temperature is shown. These sensors, properly embedded in a prototype of the vault, allow the monitoring of the corrosion process of the reinforcing steel embedded in the structure. All the information obtained from the sensors is being used for the final design of the container to achieve a service life greater than the foreseen durability for this type of facilities (more than 300 years).

Keywords: concrete vaults; corrosion; embedded sensors; intermediate-level radioactive waste; reference electrodes

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## INTRODUCTION

Since its creation in 1950, the Argentine Atomic Energy Commission (CNEA) has been working on the development of nuclear energy applications for peaceful purposes. This work includes research and development of basic and nuclear technology areas, the operation of important facilities in charge of the production of radioisotopes for medical and industrial applications and the performance of tasks in connection with the nuclear fuel cycle, mining and uranium processing activities, manufacturing of fuel elements, production of heavy water, and the operation of two nuclear power plants. As a result of such activities various types of radioactive waste have been, and are being produced. Such radioactive waste is classified according to their radioactivity level, half life and disposal technology.

The National Radioactive Waste Management Programme is in charge of evaluating and developing different alternatives for the final disposal of radioactive waste, taking into account technical, operational and financial factors. In the case of ***Intermediate Level and Short Level Radioactive Waste*** (IRLW) the proposed model is the near-surface monolithic repository similar to that in operation in El Cabril, Spain. The design of this type of repositories is based on the use of multiple, redundant and independent barriers in which the waste is immobilized in cementitious matrixes and packed in 200 liter drums or in special concrete containers. The model foresees a period of 300 years of institutional post-closure control.

The engineered barriers can be grouped in two major categories: physical barriers to prevent intrusion of water, biota or fauna and the release of radio nuclides to the environment; and chemical barriers to restrict radio nuclides migration by adsorption and ion-exchange once soluble radio nuclides are released from the source. The barriers that will be used in the near surface repository include: waste forms, disposal containers, backfill and buffer materials, reinforced concrete vaults, cover and geological medium. Since vaults and covers, made with reinforced concrete, are major components of the engineered barriers, the durability of the concrete is an important aspect for the integrity of the facility [1]. Several projects are involved concerning the durability of the facilities, and one of them is related to the concrete to be used in the engineering of the repository, as well as, to the manufacture of the containers (to hold the drums with conditioned waste), which will be disposed into the concrete vaults. For these reasons a research programme on concrete durability was initiated several years ago. The research and development are focused 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. Durability prediction requires an accurate description of the physical and chemical environment characteristics. Durability is influenced by the environment to which the concrete is exposed to, by the quality of the constituents and their proportion in the mixture design and by structural designs and construction techniques, among other factors.

Reinforcing steel corrosion is one of the degradation processes that may cause reduction and premature termination of the nuclear waste disposal facilities service life. Extensive research has been published in this field; however, very few of these studies address the specific demands required for this type of application. The present experience with modern reinforced concrete is much shorter than the expected life of the ILRW concrete disposal. This fact requires extrapolation of short term experience to 300 years foreseen life [2].

This work shows laboratory and field investigations performed during the last six years on concrete specimens containing reinforcing steel segments 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 ions and carbon dioxide, was also determined. In addition, a full scale (1:1) concrete vault was constructed and instrumented in order to monitor the evolution of the reinforcing steel corrosion rate in time.

Additionally, the development of an integrated sensor system based on the measurements of temperature inside the structure, the corrosion potential of reinforcing steel, the corrosion current density of reinforcing steel, the electrical resistivity of concrete, the availability of oxygen and the chloride ions concentration in concrete is shown. These sensors, properly embedded in a structure that simulates the vaults and containers, allow the monitoring of the corrosion process of the reinforcing steel embedded in the structure. All the information obtained from the 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.

## EXPERIMENTAL TECHNIQUE

The study was performed using concrete specimens, 20 cm high and with a square section of 10 cm per side, containing reinforcing steel segments. Each specimen contained 3 reinforcing steel segments. The reinforcing steel was 8 mm in diameter and presented an exposed area of 30 $cm^2$. The chemical composition of the reinforcing bars used in the study was 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 reinforcing steel was isolated with epoxy resin in order to avoid crevice corrosion. The reinforcing steel segments were positioned in such a way that a 2 cm concrete cover was achieved. Each specimen contained an activated titanium ($Ti/TiO_2$) internal reference electrode (IRE) with a diameter of 3.8 mm and 50 mm long located in its centre.

The concrete used in this study was developed by the Construction Center of the National Institute of Industrial Technology (INTI, Argentina) at the end of the 90´s decade. It was selected based on the concrete mechanical properties, water permeability tests and workability. These results have been published elsewhere [1, 3]. The composition of the mixture proportion was as follows: water-cementitious ratio (w/cm), 0.34; cement content (sulphate resistant cement), 410 $kg/m^3$; coarse aggregate, with maximum size of 19 mm, 1040 $kg/m^3$; fine aggregate, 810 $kg/m^3$; superplastisizer, 1-2.5%; entrapped air, 2-3%. Before casting the specimens, concrete was passed through a mesh with a hole-size of 6.35 mm (1/4"). Specimens were cured for 7 days covering the exposed concrete surface with a plastic foil. Compressive strength evaluated after 28 days ranged from 50 and 54 MPa. In the last years, new concretes have been proposed for this application, that include supplementary cementitious materials such as silica fume, fly ash, etc., to decrease permeability and/or crack susceptibility. The behavior of these materials is the objective of present investigations.

A total of 18 specimens for corrosion testing were made. After a conditioning period of 100 days the specimens were exposed to three different conditions: partially immersed in a 3.5 % NaCl aqueous solution; immersed in a 5 % $Na_2SO_4$ aqueous solution and exposed to natural carbonation in the laboratory atmosphere (room temperature and 60-70% relative humidity).

The electrochemical parameters normally used to characterize the corrosion behavior of reinforcing steel in concrete were monitored periodically during approximately 2100 days. These parameters included the corrosion potential ($E_{corr}$), the corrosion current density ($I_{corr}$) obtained from polarization resistance ($R_p$) measurements and the electrical resistivity of concrete ($\rho$) determined from resistance measurements between two reinforcing steel segments.

The $E_{corr}$ values were measured using a high input impedance voltmeter connected to the IRE. These measurements were then corrected against a copper/saturated copper sulphate reference electrode (Cu/SCS). The results where evaluated according ASTM standard C876 [4]. $R_p$ was evaluated as $\Delta V/\Delta I$ [5] from potential sweep within $E_{corr} \pm 0.01$ 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 reinforcing steel corrosion current density ($I_{corr}$) according to the Stern-Geary relationship as follows: $I_{corr}=B/R_p$, where B values should take into account whether the steel segments are in the active or passive state [6]. Finally, the concrete electrical resistance ($R_s$) was measured between bars using an earth ohm-meter. These values were used to estimate the electrical resistivity of the concrete as $\rho=k.R_s$, where $R_s$ is the geometric cell constant measured experimentally (k=27.5 cm).

Chloride concentration profiles for cylindrical concrete specimens, 10 cm in diameter and 10 cm height and partially immersed in 3.5% NaCl solution, were obtained after 1750 days exposure. In order to analyze the chloride transport mechanism in concrete, the effective diffusion coefficient ($D_{ef}$) was determined by solving Fick´s second law. The carbonation depth was determined using the phenolphthalein test after a 2350 days exposure.

Additionally, several IRE were embedded in a full scale (1:1) concrete vault in order to monitor the corrosion potential of the reinforced bars. The monitoring has been followed up for the last three years, and it will be continued for the next years.

## RESULTS AND DISCUSSION

The measurement of $E_{corr}$ as a function of the exposure time (up to 2100 days) on specimens exposed to laboratory environment showed values more positive than -0.200 $V_{Cu/SCS}$ revealing a passive state (Fig. 1). The reinforcing steel corrosion potentials measured on specimens immersed in 3.5% NaCl aqueous solution, immediately after exposure, showed values in the range -0.150 $V_{Cu/SCS}$ to –0.325 $V_{Cu/SCS}$. The $E_{corr}$ values showed increasing trends after the first 350 days exposure and after 450 days exposure reaches an $E_{corr}$ value higher than –0.200 $V_{Cu/SCS}$ (passive state). Finally, the corrosion potential of specimens immersed in 5% $Na_2SO_4$ aqueous solution showed that the behavior is similar to that observed on specimens immersed in the NaCl solution: the initial corrosion potential ranged between –0.150 $V_{Cu/SCS}$ and -0.300 $V_{Cu/SCS}$ and an almost constant value is reached after 550 days exposure. The values of $E_{corr}$ for the three exposure conditions after 2100 days are: 0.05 $V_{Cu/SCS}$ for laboratory environment; -0.140 $V_{Cu/SCS}$ when exposed to 3.5% NaCl solution and -0.225 $V_{Cu/SCS}$ were exposed to 5% $Na_2SO_4$ solution.

The reinforcing steel corrosion current density ($I_{corr}$) remained almost constant and close to $10^{-8}$ $A.cm^{-2}$ during the first 2100 days of exposure at each testing condition (Fig. 2). These results are a clear indication that steel presents a passive state although the current density of specimens immersed in aqueous solutions is almost three times higher than that exposed to laboratory environment.

The evolution of the electrical resistivity of concrete (ρ) exposed to different conditions showed that, in all conditions, the values measured increase with the exposure time. This is an indication of the continuous concrete curing process which results in a pore size distribution reduction. As could be expected, specimens exposed to the laboratory atmosphere showed the highest ρ values, reaching almost 2.5 MΩ.cm after

2100 days of exposure. On the other hand, the electrical resistivity of specimens immersed in NaCl and $Na_2SO_4$ solutions were very similar one to each other, showing values between 10 and 20 kΩ.cm after 2100 days of exposure.

After measuring the total chloride concentration profiles obtained from specimens partially immersed in 3.5% NaCl aqueous solution during 1750 days, the following values of the chloride effective diffusion coefficient ($D_{ef}$) and chloride surface concentration values ($C_s$) were obtained: $2.75 \times 10^{-12}$ $m^2.s^{-1}$ and 2.64 % (cement base), respectively. These values correlate well with those reported by Bamforth [7] for marine structures (extreme conditions). No evidence of carbonation was observed on concrete after an exposure period of 2350 days (6.4 years). The constant K in the equation $x=K.t^{0.5}$, x being the carbonation depth and t the exposure time, is lower than 0.395 $mm.years^{-0.5}$, taking into account an x detection limit of 1.0 mm.

Figure 3 shows the evolution of the corrosion potential as a function of time, for corrosion probes embedded in the full scale (1:1) container. It can be shown that, up to now, reinforcing steel remains passive, with corrosion potential values higher than the potential limit for passivity breakdown (-0.2 $V_{Cu/SCS}$).

According to the threshold values of $E_{corr}$ and $I_{corr}$ for the passive to active transition for steel corrosion in concrete ($E_{corr} < -0.35$ $V_{Cu/SCS}$ and $I_{corr} > 0.1$ $\mu A.cm^{-2}$), the results obtained in laboratory and in field show that, in all cases, the steel reinforcement remains in the passive state. The service criterion proposed by Andrade and Alonso [2] for reinforced concrete in ILRW facilities assumes that the durability of these structures ends once the reinforcing steel corrosion has been initiated. According to Tuuti´s service life model [8], no propagation period must be considered. In order to fulfill this criterion, the concrete must be designed to completely avoid corrosion during the period of almost 300 years. Two consequences of this statement are: ILRW facilities must not be located in places where chlorides, sulphates or the carbonation front could reach the reinforcing steel during the service life of the structure and, 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.

It is worth mentioning that the site for the near surface disposal facility in the Argentine Republic has not yet been determined. 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 next most important cause of reinforced corrosion is the carbonation during the period in which the vaults are kept in contact with air [9]. Taking into account the diffusion rate of $CO_2$ in concrete, after 300 years, the carbonation depth would be less than 7 mm, that is to say, much less than the concrete cover thickness. Then, it is expected that the concrete under study fulfills the requirements for the foreseen life-time. Besides, in the present work, the influence of both chloride and sulphate ions on the corrosion behavior of reinforcing steel was studied taking into account the remote possibility of accidental contaminations. Finally, it is important to point out that after the selection of the site for the near surface disposal facility, new tests will be carried out to evaluate the service life of the concrete and its behavior in the environment of the repository.

## DEVELOPMENT OF EMBBEDED SENSORS

The electrodes proposed as reference electrodes to be embedded in concrete for a long time were made from metal-metal oxide (MMO) activated titanium rod (ATR) stock 3-mm dia. commercially produced for permanent impressed-current anodes in cathodic protection of reinforcing steel in concrete. The surface of the ATR was covered with a precious mixed-metal oxide applied using a proprietary process. Energy-dispersive x-ray spectroscopy (EDS) of the ATR coating identified Ir and Ta as the main metallic species. The electrodes were prepared by cutting the rod in 5-cm segments, drilling a 1-mm dia. hole 6 mm in depth at one end, and crimping the stripped end of an insulated braided Cu cable in the hole. The crimped and opposite ends of the bar were covered by epoxy resin. A complete electrochemical study of this ATR electrode was performed in order to determine its ability to be used as reference electrode [10].

The specific chloride electrodes were made with a 50 mm long silver wires (99.99% pure), 2 mm in diameter, soldered onto a low noise screened cable. A 1 cm heat shrink tubing was cut and fitted over the connection between the silver wire and the cable. The silver wire was then subject to an anodic treatment to produce a stable film of AgCl. The specific chloride electrode so manufactured above was tested in KCl solutions with concentrations ranging from $10^{-5}$ to 1 M in order to determine the calibration curve. The results shows a quite good linear fit between the electrode potential and the logarithm of chloride concentration with an slope close to that predicted by the Nerst equation (-0.063 ±0.003).

The oxygen availability is obtained by recording the current density measured after 300 s when a 6 mm dia 316L stainless steel rod is polarized at -0.950 $V_{(\text{ATR electrode})}$ using a similar stainless steel rod as a counter electrode. The current density (I) is then converted into oxygen flux by using the Faraday’s Law.

The concrete electrical resistivity is measured by applying a sinusoidal signal ($\Delta V$= 10 mV, $\nu$=1 kHz) between two identical 316L stainless steel rods (6 mm dia.), and computing the value of the resistance ($\Omega$). The cell constant is obtained by measuring, with this technique, the resistance of a series of solutions of known resistivity (KCl solutions with concentrations ranging from $1 \times 10^{-5}$ to 1M).

The corrosion potential ($E_{corr}$) is measured on a 5 mm dia. black steel rod, while the corrosion rate is obtained by cathodically polarizing this rod at a preselected current density ($I_{appl}$) and measuring the potential of the rod (E) after a certain period of time. The polarization resistance ($R_p$) is obtained as:

$$R_p = -\frac{E - E_{corr}}{I} - R_s$$

where $R_s$ is the solution resistance measured as mentioned above. The corrosion rate was calculated by applying the equation $I_{corr}=R_p/B$, where B is a constant, which in the present case has been given a value of 0.026 V [11].

The temperature is measured with a conventional platinum resistance thermometer (Pt 100 type) protected from the environment using 316L stainless steel as sheath material.

All the above mentioned electrodes and the thermometer were embedded in a special epoxy resin, resistant to the alkaline environment, and the exposed part of the electrodes (and thermometer) were then covered with a repair mortar and then attached to the reinforcing steel cage (in the case of a new structure) or embedded inside an existing structure.

The sensor is connected via an 8-pin connector to a control case, and this case is connected via USB port with a notebook which has a software named HormiCor 400, developed specifically for this purpose, that makes possible to programme the sequence of measurements and generates a system of alarms when the recorded value exceeds a previously determined value. As regards the measurement methods, temperature, corrosion potentials—of the probe and the reinforcing steel cage—and the potential of the specific chloride electrode are simple recordings of the response generated by the sensor. For the measurement of the concrete electrical resistivity, corrosion current density and oxygen flux, it is necessary to generate a signal disturbing the sensor and the response to this induced disturbance is recorded and used to compute the desired parameters.

Up to now, this system has been embedded in a simulated wall of a concrete vault for intermediate-level radioactive waste disposal and in the spillway of a dam in the south of the Argentine Republic. The results obtained so far are promising and allow the follow up of the state of the structures from the reinforcing steel corrosion point of view.

## CONCLUSIONS

a) The concrete made of sulphate resistant cement provides a passive status of corrosion to reinforcing steel characterized by corrosion rates lower than 0.1 $\mu A.cm^{-2}$ (≈ 1 $\mu m.year^{-1}$), assuming low levels of chloride and sulphate ions.

b) The values of the chloride effective diffusion coefficient ($D_{ef}$) and the chloride 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.

c) To guarantee a 300 years service life, the reinforcing steel corrosion rate on intermediate level radioactive waste 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.

d) 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.

e) In order to fully evaluate the behavior of concrete durability from the reinforcing steel corrosion point of view, 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.

f) Durable, embeddable and inexpensive sensors for monitoring the corrosion process of new and existing reinforced concrete structures were developed.

g) The sensors provide *on-line* information of the corrosion potential and the corrosion rate of the reinforcing steel, the concrete electrical resistivity, the oxygen availability, the chloride content and the temperature inside the structure. Besides, the software generates a system of alarms that allows the specialist to make a decision concerning what mitigation strategies to apply.

h) Results from sensors installed over the past months are promising because they show changes as the concrete cures and dries out in new structures.

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