

Corrosion susceptibility of steel drums to be used as containers for intermediate level nuclear waste

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Abstract. The present work is a study of the corrosion susceptibility of steel drums in contact with cemented ion-exchange resins contaminated with different types and concentrations of aggressive species. A special type of specimen was manufactured to simulate the cemented ion-exchange resins in the drum. The evolution of the corrosion potential and the corrosion rate of the steel, as well as the electrical resistivity of the matrix were monitored over a time period of 900 days. The aggressive species studied were chloride ions (the main ionic species of concern) and sulphate ions (produced during radiolysis of the cationic exchange-resins after cementation). The work was complemented with an analysis of the corrosion products formed on the steel in each condition, as well as the morphology of the corrosion products. When applying the results obtained in the present work to estimate the corrosion depth of the steel drums containing the cemented radioactive waste after a period of 300 years (foreseen durability of the Intermediate Level Radioactive Waste facility in Argentina), it is found that in the most unfavourable case (high chloride contamination), the corrosion penetration will be considerably lower than the thickness of the wall of the steel drums.

1 Introduction

The main wastes arising during the operation of a nuclear power plant are components which are removed during refuelling or maintenance (activated solids such as stainless steel containing cobalt-60 and nickel-63) or operational wastes such as radioactive liquids, filters, and ion-exchange resins which are contaminated with fission products from circuits containing liquid coolant. Ion-exchange resins constitute the most significant fraction of the wet solid waste produced at power reactors. The ion-exchange material may be regenerated after having reached saturation of the active groups, or may be removed as waste concentrate to be solidified. Immobilization processes involve the conversion of the wastes to chemically and physically stable forms that reduce the potential for migration or dispersion of radionuclides. If possible, volume reduction should also be a matter of concern.

The design of the Intermediate Level Radioactive Waste repository in Argentina foresees a period of 300 years of institutional post-closure control. In this model, wastes are immobilized in cement

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matrixes and packed in 200-litre drums with an extra enclosure made of concrete to guarantee the radionuclides containment. Depending on the conditions the drum may undergo internal corrosion due to the presence of contaminants in the waste. As a consequence of a conservative approach to the safety analysis, the steel drums are not considered to be physical barriers, with the concrete assumed to be the sole barrier to prevent radionuclide release during the life-span of the facility. However, if the durability of the steel drums could be guaranteed, an extra security period could be claimed.

The present work is a study of the corrosion susceptibility of steel drums in contact with cemented ion-exchange resins contaminated with different types and concentrations of aggressive species. To achieve this aim, a special type of specimen was manufactured to simulate the cemented ion-exchange resins in the drum [1]. The evolution of the corrosion potential (E_{corr}) and the corrosion rate (CR) of the steel, as well as the electrical resistivity (ρ) of the matrix were monitored over a time period of 900 days. The aggressive species studied were chloride ions (the main ionic species of concern) and sulphate ions (produced during radiolysis of the cationic exchange-resins after cementation [2-3]). The work was complemented with an analysis of the corrosion products formed on the steel in each condition, as well as the morphology of the corrosion process.

2 Experimental technique

The specimens used were manufactured to simulate cemented ion-exchange resins in the drums (Figure 1). Each specimen consists of a sheet of the steel used to manufacture the drums (0.9 mm in width), 6x6 cm² in area, and a PVC tube (4.5 cm in diameter and 7.0 cm in height) attached to the steel sheet by a epoxy putty used for sanitary repairs. The chemical composition of the steel is as follows (%wt): C, 0.069%; Si, 0.08%; Mn, 0.43%; P, 0.009%, S, 0.005%, Fe, balance. This composition corresponds to a steel SAE 1006. The steel drums are usually painted both inside and outside, though in this study the steel was used with no coating. A graphite bar, 1.2 cm in diameter, was used as counterelectrode, and a titanium bar activated with mixed-metal oxide (MMO) was used as reference electrode. The behaviour of this type of reference electrode in concrete was previously studied [4-5].

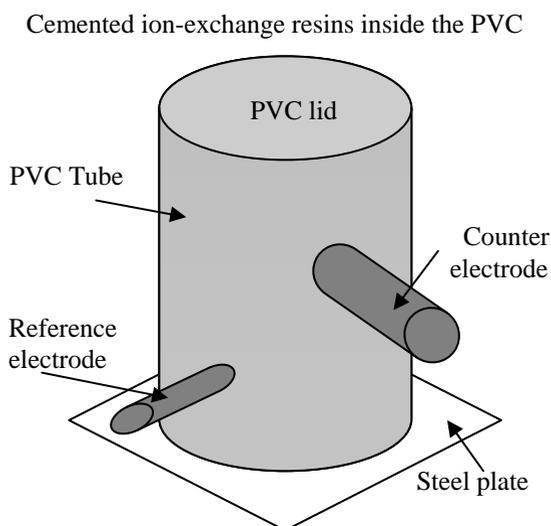


Fig. 1. Diagram of the specimen used to simulate the cemented ion-exchange resins in the steel drums.

After sealing with the putty, the cemented waste forms, prepared as described below, were placed inside the tube. Finally, a PVC lid was put on the tube in order to avoid the access of oxygen to the specimen. The specimens, so prepared, were left exposed to laboratory conditions, where the

temperature is 24.1 ± 2.9 °C. The simulation of exhausted ion-exchange resins was made by mixing Cationic Resin Lewatit® S100 KR/H+ and Anionic Resin Lewatit® M500 KR/OH- of Bayer Chemicals, in a proportion equal to 1.137 (in weight) with an aqueous solution containing 15% w/w of NaNO₃ and 3.7 % w/w of NaOH (both analytical grade). In this way, the quantity of anions and cations present in solution is enough for complete saturation of the resins. After a 24-hour saturation period (stirring periodically), the supernatant liquid was removed and the resins were rinsed 5 times with ultra pure water. The resulting product was mixed with cement (Ordinary Portland Cement CPN 40 ARS, Loma Negra®) and water, according to standards ASTM C-305 and AASHTO T-162 for the preparation of mortars. The final mix has the following composition: ion-exchange resins (by weight of dry components) 14.2%; cement 56.8% and water, 29%. The final formulation has a water/cement (w/c) ratio equal to 0.51.

To evaluate the corrosion resistance of the steel under different aggressive conditions, four different sets of specimens were prepared. The first set contains no aggressive species in the formulation. The second and third sets contain NaCl added to the mix in two proportions: 0.5% and 5% of chloride ions with respect to the cement mass, respectively. The fourth set contains Na₂SO₄ at a concentration of 2.3% of sulphate with respect to the cement mass. The introduction of sulphate ions represents the situation in which cationic resins, that have sulphonic groups in their structure, are damaged by radiolysis and release sulphate ions to the system. The sulphate concentration used in the present work represents the maximum quantity of sulphate ions that can be released under γ -radiation, and corresponds to 33% degradation of pure cationic resins [3]. Prismatic specimens were prepared for mechanical tests (compressive strength 18.9 ± 2.2 MPa, and flexural strength 4.4 ± 0.8 MPa).

The electrochemical parameters normally used to characterise the corrosion behaviour of steel in contact with cementitious materials were monitored periodically: the ρ of the cemented waste forms determined from resistance measurements between the steel sheet and the MMO reference electrode; the E_{corr} of the steel measured against the MMO reference electrode; and the CR obtained from polarisation resistance (R_p) measurements by means of the linear polarisation resistance technique and the application of the Stern-Geary relationship [6]. Repetitive results were obtained in all cases and, for the sake of simplicity, only representative values are reported in the results section. The potentials are reported in the copper/saturated copper sulphate reference electrode scale (CSE) according to a previously determined relationship [4-5].

After 900 days test, the steel sheets were broken apart from the specimens and observed with both, optical (Olympus BX60M) and scanning electron microscope (SEM, Quanta 200). Energy Dispersion X-ray analysis (EDAX) was performed at many locations of the steel sheet and in the cementitious matrix to assess the local chemical composition. After removing the rust scale in a 10% ammonium citrate solution at 60 °C (descaling), the steel sheets were observed again under the SEM. Metallographic cross sections of both, non-descaled and descaled specimens were prepared by cutting small pieces of the sheets, and mounting them in curing epoxy at room temperature. Additionally, corrosion products were analyzed by Transmission Mössbauer Spectroscopy (TMS). In this case, the analysis was performed using a ⁵⁷Co source in a Rh matrix. Spectra were collected at room temperature (RT). Analysis of the spectra was performed using the Normos least-squares fitting program [7]. Isomer shift values are given relative to α -Fe at room temperature.

3 Results and discussion

In figure 2 it is shown that the matrix ρ has a tendency to increase with time, which reflects the continuous hydration process showed by the system. Although the increase in ρ is continuous, there is a change in the slope at about 350 days of exposure. In all cases, by the end of the tests (900 days) the values of ρ lie between 500 and 1000 kohm.cm. These values, according to Andrade and Alonso, imply negligible corrosion because the matrix is too dry [8].

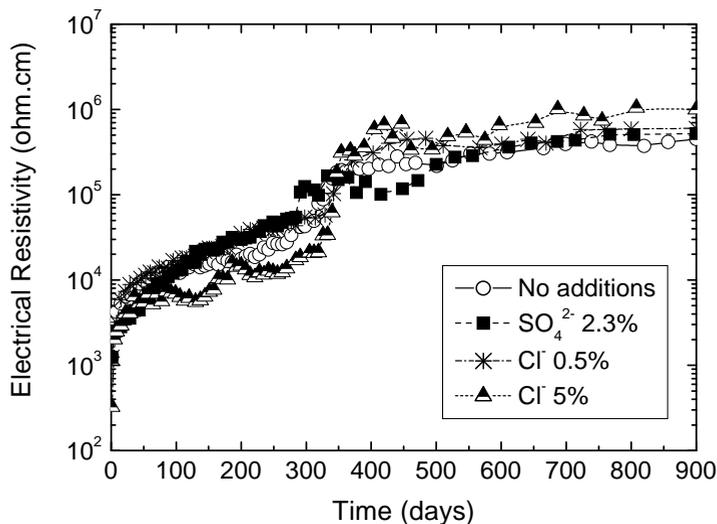


Fig. 2. Matrix electrical resistivity (ρ) as a function of time.

In figure 3 it is shown that, in the case of no aggressive ion additions to the mix or when sulphate ions are added, the E_{corr} remains stable during the 900 days of exposure. Additions of 0.5% chloride ions shift the E_{corr} towards more negative values but, after about 350 days, E_{corr} increases and at 900 days reaches a value close to those obtained with no contaminant additions. Specimens with the addition of 5% chloride show the lowest E_{corr} immediately after the start of the test. This value remains almost constant for 350 days and afterwards increases slowly. According to ASTM C-876 standard [9], steel plates in contact with non-contaminated matrix or with the addition of sulphate ions are in a passive state (E_{corr} higher than $-0.2 V_{\text{CSE}}$) with a very low corrosion probability. Steel plates in contact with a matrix highly contaminated with chloride (5%), are in the active state (E_{corr} lower than $-0.35 V_{\text{CSE}}$) from the beginning of the test up to about 350 days, with a very high corrosion probability. Then, E_{corr} increases reaching values at which, according to the standard, the probability of corrosion is uncertain (E_{corr} between $-0.35 V_{\text{CSE}}$ and $-0.2 V_{\text{CSE}}$). Finally, in the presence of 0.5% chloride ion concentration, the probability of corrosion is uncertain from the beginning of the test up to about 350 days, when the steel plates passivate.

CR were calculated using the expression $CR = k \cdot B / R_p$ where B is a constant that depends on the active/passive state of the steel: B is equal to 0.026 V, in the case the steel is in the active state, and 0.052 V in the case of passive state [10]. k is a constant that relates corrosion current densities and CR by applying Faraday's Law [$k = 11.6 (\mu\text{m}/\text{year}) / (\mu\text{A}/\text{cm}^2)$]. Results are shown in figure 4. In the case of formulations with no additions, or with the addition of sulphate, the CR slowly decreases from less than 1 $\mu\text{m}/\text{year}$ to about 0.01 $\mu\text{m}/\text{year}$. These values are consistent with the values of E_{corr} that indicate a passive state of the steel. On the other hand, in matrixes with additions of 0.5% chloride ions, the CR increases with time during the first 100 days to reach a value close to 10 $\mu\text{m}/\text{year}$, and then slowly decreases reaching a value of 0.4 $\mu\text{m}/\text{year}$ after 900 days of exposure. Finally, for 5% chloride addition, the CR values show a sharp increase during the first 300 days reaching a value close to 1 mm/year. Afterwards, the CR starts to decrease monotonically reaching, at the end of the test, a CR value close to those obtained in matrixes with no-additions, or with the additions of sulphate ions. In all cases, after 900 days, the steel plates behave as if they were passivated (no matter the additions of aggressive species) with a low or negligible CR [11].

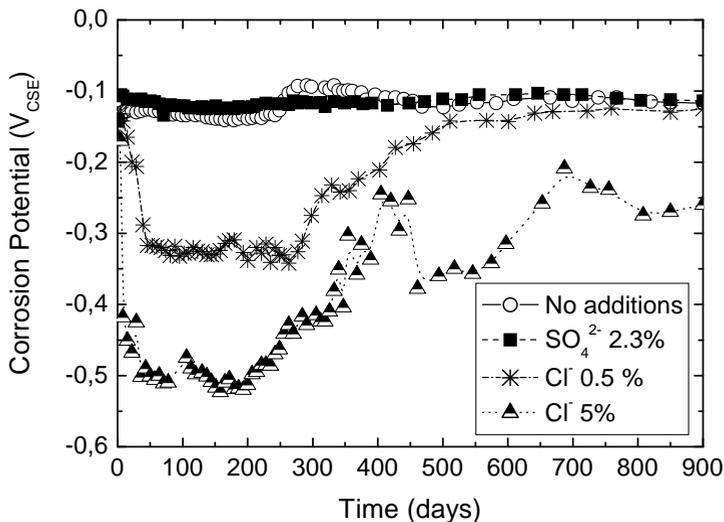


Fig. 3. Corrosion potential (E_{corr}) as a function of time.

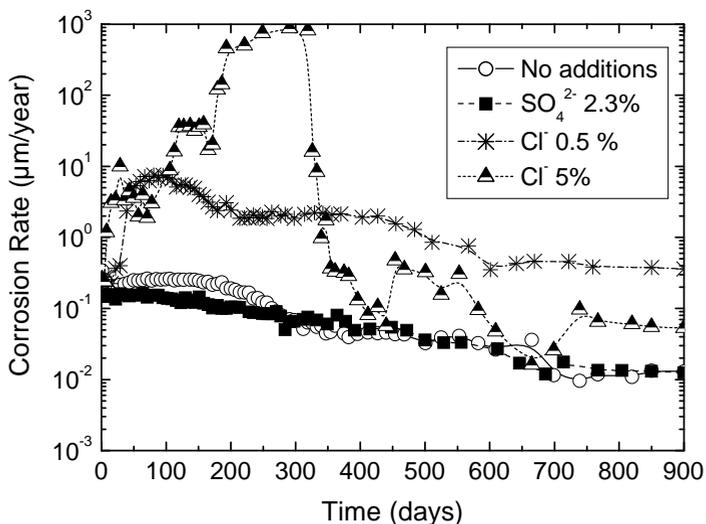


Fig. 4. Corrosion rate as a function of time.

After the tests, the plates were observed under the SEM. Specimens with no additions and the addition of 2.3% sulphate, show that steel is covered with white products, that are remains of the cementitious matrix (determined by EDAX), with no corrosion products. Steel plates of the specimens with the addition of 0.5% chloride reveal the presence of corrosion products of different morphologies: compact corrosion products with cracks, grown over crystals showing fine plates (“flowery” structures), probably due to lepidocrocite (γ -FeOOH). With the addition of 5% chloride corrosion products of different morphologies were observed. Figure 5.a shows needle-like crystals corresponding to whiskers of goethite (α -FeOOH). Figure 5.b shows a globular (“cotton-ball”) pattern, typical of akaganeite (β -FeOOH). In Figure 5.c, a first formed amorphous layer appears as a

sedimentary soil layer in which cracks develop during drying. On top of this layer, circular grains showing bulges appear as donuts, corresponding to magnetite (Fe_3O_4) [12-14].

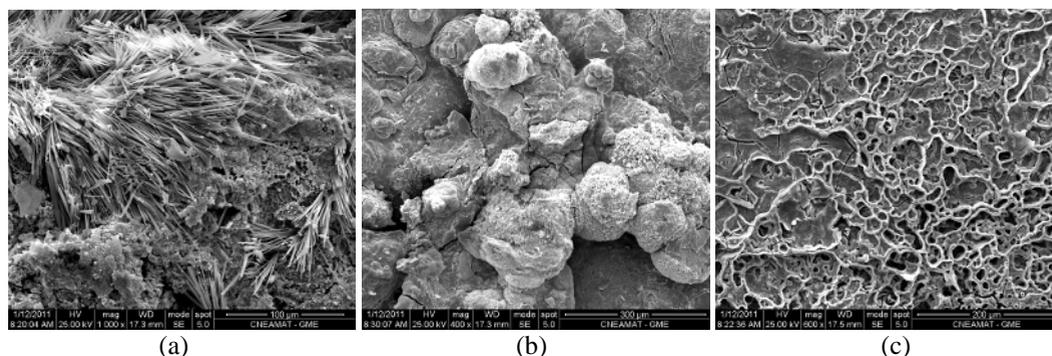


Fig. 5. SEM micrographs of steel plates after tests with the addition of 5% chloride.

Metallographic cross sections of the specimens exposed to 5% chloride addition showed, both, general and pitting attack (Figure 6). Mössbauer spectroscopy of the corrosion products revealed that akaganeite was the main compound. Magnetite and/or non stoichiometric maghemite, goethite and hematite were also found in the spectra in lower concentrations.

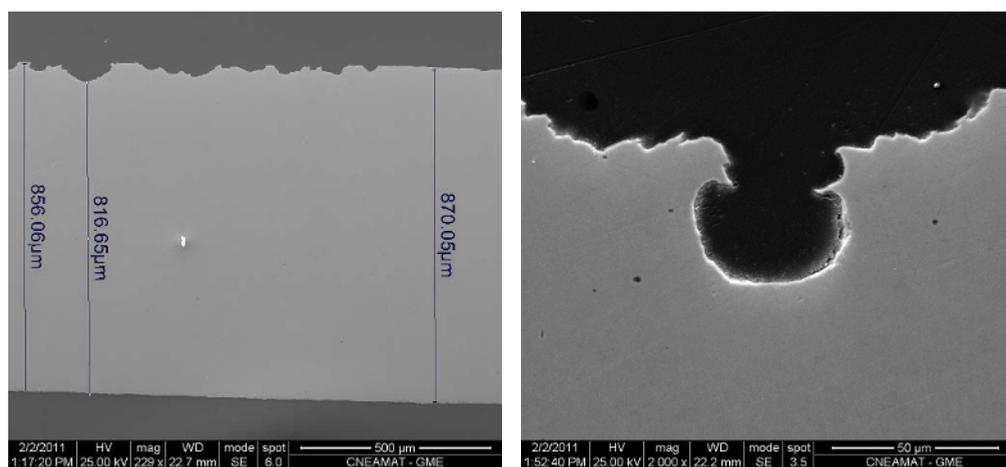


Fig. 6. Metallographic cross sections showing the morphology of the attack. 5% chloride addition.

From the metallographic cross sections, the thickness of the remaining steel plate was measured and the depth of the corrosive attack was determined by subtracting these values from the original thickness of the steel plates. In those specimens exposed to 5% chloride addition, the maximum depth of the corrosive attack is 150 μm . Taking into account that the test duration was 900 days, the average CR at that location is about 60 $\mu\text{m}/\text{year}$. Besides, from Figure 4, it is evident that the CR in the case of 5% chloride addition, is only significant during the first year of exposure. After 1 year, the CR drops abruptly reaching a value close to 0.1 $\mu\text{m}/\text{year}$. This implies that most of the 150 μm of corrosive attack must have occurred during the first year. When applying these results to estimate if the durability of the steel drums will be higher than the foreseen life-span of the facility (300 years), the following computation should be done: the maximum depth of the total corrosive attack would be 150 μm (that would occur during the first year of exposure) plus the corrosion penetration that would occur during most of the rest of the time. Assuming a constant CR of 0.1 $\mu\text{m}/\text{year}$ from the first year of exposure and during most of the life-span of the facility, this last contribution would yield about 30 μm . As a consequence, it would not be expected a total corrosion penetration higher

than 180 μm . Taking into account that the thickness of the wall of the steel drums is 0.9 mm, it is predicted that the durability of the steel drums will be higher than the foreseen life-span of the facility so, its durability is guaranteed. It is worth mentioning that these values correspond to the most conservative approach, because calculations were performed for the most concentrated chloride condition.

The fact that the CR values decrease abruptly as a function of time in the tests performed with 5% chloride additions is believed to be due to the lack of water necessary for the corrosion process to occur. This assumption is validated when the evolution of the ρ of the matrixes (Figure 2) is taken into account. After almost 350 days test, the resistivity underwent a change in the slope as a function of time, reaching suddenly values close to 300 kohm.cm. This means that the conductivity of the media is very low due to the lack of water that was consumed by the cement hydration process. According to Andrade et al. [11] when the resistivity of concrete (or a cementitious matrix) is higher than 100-200 kohm.cm, the CR is negligible due to a very dry matrix. Then, the conclusion is that, the decrease of the CR with time, after reaching a high CR value, is due to the dryness of the matrix that hinders the development of the corrosion process, no matter the high concentration of aggressive species and the presence of oxygen.

4 Conclusions

From the present work the following conclusions can be drawn:

The corrosion rate of the steel in contact with cemented ion-exchange resins in the absence of contaminants or in the presence of sulphate is low (less than 0.1 $\mu\text{m}/\text{year}$) during the whole period of the study (900 days).

The corrosion rate of the steel increases with the presence of chloride ions at the beginning of the exposure but, after 1 year, the corrosion rate drops abruptly reaching a value close to 0.1 $\mu\text{m}/\text{year}$. This is probably due to the lack of water to sustain the corrosion process.

When applying the results obtained in the present work to estimate the corrosion depth of the steel drums containing the cemented radioactive waste after a period of 300 years, it is found that in the most unfavourable case (high chloride contamination), the corrosion penetration will be considerably lower than the thickness of the wall of the steel drums. Thus, cementation of ion-exchange resins seems not to pose special risks regarding the corrosion of the steel drums that contained them; even in the case the matrix is highly contaminated with chloride ions.

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