



## Corrosion susceptibility of steel drums containing cemented intermediate level nuclear wastes

Gustavo S. Duffó<sup>a,b,c</sup>, Silvia B. Farina<sup>a,b,\*</sup>, Fátima M. Schulz<sup>a</sup>, Francesca Marotta<sup>d</sup>

<sup>a</sup> Consejo Nacional de Investigaciones Científicas y Técnicas, Av. Gral. Paz 1499 – (1650) San Martín, Buenos Aires, Argentina

<sup>b</sup> Universidad Nacional de San Martín, Av. Gral. Paz 1499 – (1650) San Martín, Buenos Aires, Argentina

<sup>c</sup> Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499 – (1650) San Martín, Buenos Aires, Argentina

<sup>d</sup> Politecnico di Milano, Piazza Leonardo da Vinci 32 – (20133) Milano, Italy

### ARTICLE INFO

#### Article history:

Received 8 June 2010

Accepted 13 August 2010

### ABSTRACT

Cementation processes are used as immobilization techniques for low or intermediate level radioactive waste for economical and safety reasons and for being a simple operation. In particular, ion-exchange resins commonly used for purification of radioactive liquid waste from nuclear reactors are immobilized before being stored to improve the leach resistance of the waste matrix and to maintain mechanical stability. Combustible solid radioactive waste can be incinerated and the resulting ashes can also be immobilized before storage. The immobilized resins and ashes are then contained in steel drums that may undergo corrosion depending on the presence of certain contaminants.

The work described in this paper was aimed at evaluating the corrosion susceptibility of steel drums in contact with cemented ion-exchange resins and incineration ashes containing different concentrations of aggressive species (mostly chloride and sulphate ions). A special type of specimen was designed to simulate the cemented waste in the drum. The evolution of the corrosion potential and the corrosion current density of the steel, as well as the electrical resistivity of the matrix were monitored over a time period of 1 year. The results show the deleterious effect of chloride on the expected lifespan of the waste containers.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

The National Atomic Energy Commission (CNEA) of the Argentine Republic works on the development of nuclear energy applications for peaceful purposes. The tasks include, among others, the research and development of nuclear technology, the operation of important facilities responsible for 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, and the operation of two nuclear power plants. As a result of such activities performed in the nuclear field by CNEA and other private and public entities, various types of radioactive waste are being produced.

The radioactive waste is classified according to its radioactivity level, half-life and disposal technology and the National Radioactive Waste Management Programme is responsible for evaluating and developing different alternatives for its final disposal. In the case of Intermediate Level Radioactive Waste (ILRW) the proposed model is the near-surface monolithic repository similar to that in

operation in El Cabril, Spain. This type of repository is based on the use of multiple, redundant and independent barriers in which the waste is immobilized in cementitious matrixes and packed in 200-l drums or in special concrete containers. The model proposed for the repository must cover a timescale of more than 300 years.

Among the wastes arising during the operation of nuclear power plants are components that are removed during refuelling or maintenance, as well as liquids, that are contaminated with fission products. Liquid radioactive waste generated at nuclear power plants has to be decontaminated in order to be released to the environment or recycled. Among the technical processes available for treatment of liquid waste (i.e. evaporation, chemical precipitation/flocculation, solid-phase separation and ion-exchange), ion-exchange resins based treatments have found extensive application [1,2]. Ion-exchange resins are granular substances that have the ability to trap certain ions and release other ions, through a process called ion-exchange. They are used for purification of radioactive liquid waste and thus become contaminated with fission products. In most systems, ion-exchange processes are applied using a fixed bed of ion-exchange material contained in a column through which the contaminated effluent is passed. The ion-exchange material may be regenerated after having reached saturation of the active groups, or it may be removed as waste to be immobilized for further storage and final disposal. Immobilization

\* Corresponding author at: Universidad Nacional de San Martín, Av. Gral. Paz 1499 – (1650) San Martín, Buenos Aires, Argentina. Tel.: +54 11 6772 7403; fax: +54 11 6772 7388.

E-mail address: [farina@cnea.gov.ar](mailto:farina@cnea.gov.ar) (S.B. Farina).

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 performed. Ion-exchange resins constitute the largest fraction of the wet solid waste produced at power reactors and they are classified as ILRW.

One of the essential aims in the treatment of solid waste is to reduce the volumes to be stored and to concentrate and immobilize the radioactivity contained in the waste as much as possible. Experience has shown that between 50% and 80% of the solid radioactive waste produced at nuclear power plants can be classified as combustible waste [1]. From a number of view points incineration of this waste represents a substantial improvement over simple compaction because very high volume reduction and mass reduction can be achieved. The final product is a homogeneous ash which can be either packaged without further conditioning into containers for storage and disposal, or immobilized prior to storage in steel drums.

Cementation processes are used for immobilization for economical reasons as well as for being a simple operation [2–5], although other forms of immobilization such as bituminization and polymer encapsulation are also used [2,6]. For ion-exchange resin cementation, the main research focuses on increasing the loading of spent resins, reducing leaching of radionuclides, improving the compression strength of the matrix and controlling the heat generated by exothermic hydration reactions during cementation. As a consequence of this research, some new developments of cement solidification have appeared in the last few years [7–11]. For cementation of incineration ashes, very little information is available in the literature, except for a technical report on characterization of simulated radioactive waste ashes and evaluation of conditioning methods [12]. In this report, different contents of ashes, types of cement and proportions of water were tested, and the mechanical properties of the mixes thus obtained were evaluated. Ash contents up to 50% of the total solid mass were considered.

After immobilization, ion-exchange resins and incinerated ashes are conditioned in steel drums that, in turn, may undergo corrosion depending on the presence of certain contaminants in the waste. An extra enclosure made of concrete is required to guarantee the radionuclides containment. 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. No reference to the corrosion rate of drums under these particular conditions could be found in the literature.

The work described in the present paper is part of a systematic study of the corrosion susceptibility of steel drums in contact with cemented waste-forms (i.e. ion-exchange resins and incinerated ashes) with different types and concentrations of aggressive species. To achieve this aim, a special type of specimen was manufactured to simulate the cemented waste in the drum. The evolution of the corrosion potential and the corrosion current density of the steel, as well as the electrical resistivity of the matrix were monitored over a time period of 1 year. In the case of ion-exchange resins, 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 [13]). In the case of incinerated ashes, the aggressive species are mostly chloride ions. The deleterious influence of chloride on the corrosion of steel in cement and concrete environments is already known in the literature (i.e. see Ref. [14]). The aim of the present work is to find out the effect of chloride in a particular and complex system, in which chloride is mixed with other compounds such as those coming from incineration ashes and resins. On the other hand,

the effect of sulphate ion in the corrosion susceptibility of steel was studied because it is known that sulphate ions can induce pitting or pitting inhibition depending on the environmental conditions [15].

## 2. Experimental technique

A special type of specimen was manufactured to simulate the cemented waste in the drums, as shown in Fig. 1. Each specimen consists of a sheet of the steel used to manufacture the drums,  $6 \times 6 \text{ cm}^2$  in area, and a PVC tube (4.5 cm in diameter and 7.0 cm in height) attached to the steel sheet by a two-component epoxy putty used for plumbing 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 steel grade SAE 1006. The steel drums are usually painted both inside and outside, although in this first part of the study the steel was used in the 'as received' condition. A graphite bar, 1.2 cm in diameter, was used as a counter electrode, and a titanium bar coated with mixed-metal oxide (MMO) was used as a pseudo-reference electrode. The behaviour of this type of electrode in mortar was previously studied [16] and it is resumed as follows: it was found that the potential of these electrodes in aqueous solutions depends linearly on the pH of the solution from pH 7.4 to 13.5 with an slope of about 59 mV, being the potential at pH 13.5 equal to  $0.1 V_{\text{NHE}}$ . The potential is independent of the oxygen content of the environment which constitutes an advantage when performing potential measurements in media where local variations of oxygen are expected, as it is the case of the present work. On the other hand, this type of electrodes is recommended in those situations in which chloride is present due to its stability no matter the chloride content of the environment.

Both electrodes, the graphite and MMO, were placed inside the PVC tube as shown in Fig. 1. The counter electrode passed through the tube while the reference electrode reached the centre of the tube. After sealing with the putty, the cemented waste-forms, prepared as described below, were placed inside the tube. A PVC lid was put on the tube. After preparation specimens were left exposed to laboratory conditions, where the temperature was  $22.4 \pm 1.7 \text{ }^\circ\text{C}$  and the relative humidity was  $45 \pm 9\%$ .

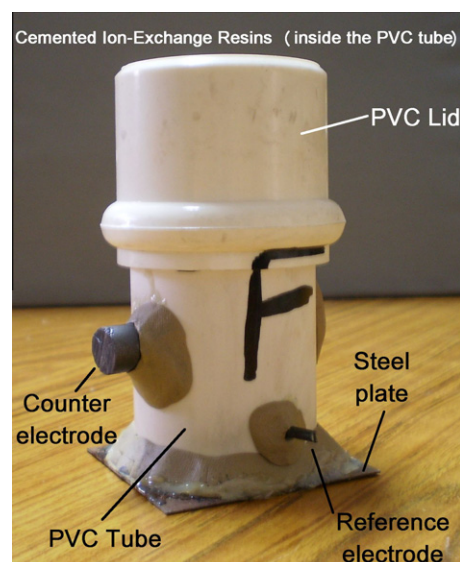


Fig. 1. Specimens designed to simulate the cemented ion-exchange resins in the steel drums.

The mix design for the ion-exchange resin cementation process used in this study was developed by experimental research performed by the National Institute of Industrial Technology (INTI) and CNEA of Argentina and it is currently the one that it is going to be used when cementation takes place. The simulation of spent ion-exchange resins was made by mixing Cationic Resin Lewatit S100 KR/H<sup>+</sup> and Anionic Resin Lewatit M500 KR/OH<sup>-</sup>, from Bayer Chemicals in a ratio 1.137:1 in weight (this ratio is the same used in the Argentinean Atucha I Nuclear Power Plant) with an aqueous solution containing 15% w/w of NaNO<sub>3</sub> and 3.7% w/w of NaOH (both analytical grade). The quantity of solution added to the resins was in the following proportion: 1.03:1 in weight. In this way, the quantity of anions and cations present in solution is enough for complete saturation of the resins. The general properties of the resins used in this work are shown in Table 1. After a 24-h 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) and water, according to the ASTM C 305–99 standard [17] for the preparation of mortars. The final mix has the following composition: ion-exchange resins (by weight of dry components) 14.2%; cement (CPN 40 ARS, Loma Negra) 56.8% and high purity water (18 MΩ cm), 29%. The final formulation had a water/cement (w/c) ratio equal to 0.51. This mix was then placed inside the PVC tubes. The composition of the cement used is shown in Table 2. The mechanical properties of the matrix obtained were: compressive strength 18.9 ± 2.2 MPa, and flexural strength 4.4 ± 0.8 MPa.

To evaluate the corrosion resistance of the steel under different aggressive conditions, four different sets of specimens were prepared. Each set consisted of six specimens, so that reproducibility was guaranteed. In summary, a total of 24 specimens, six for each condition, were made. The first set contained no aggressive species in the formulation. The second and third sets contained 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 contained Na<sub>2</sub>SO<sub>4</sub> at a concentration of 2.3 wt% of sulphate with respect to the cement mass. The introduction of sulphate ions represents the situation in which cationic resins, which have sulphonic groups in their structure, are damaged by radiolysis and release sulphate ions into the system. The sulphate concentration used in the present work represents the maximum quantity of sulphate ions that could be released under γ-radiation and corresponds to 33% degradation of pure cationic resins [13]. In addition, prismatic cement specimens were prepared for mechanical tests and microscopic observations. The pH of the final mix (ion-exchange resins plus cement plus water) was measured before pouring it inside the PVC tube. The value was about 12.5, independently of the addition of chloride or sulphate ions.

The ashes employed in the present work were prepared using analytical grade reagents, according to the chemical composition obtained from the literature [12] and shown in Table 3. This composition corresponds to ashes obtained from the incineration of plastics (including PVC), clothes, wood, paper and rubber.

The mix design for the ashes cementation specimens used in this study contained the simulated ashes, cement (of the same type detailed in Table 2) and high purity water. Due to the fact that the optimal immobilization formulation has not been determined yet, in the present work different ash contents were evaluated: 0, 10, 30 and 50% of ashes respect to total solid mass (six specimens of each formulation). In all cases the water/total solid mass ratio was kept fixed at a value of 0.5, corresponding to water/cement (w/c) ratios equal to 0.5, 0.55, 0.71 and 1, for each one of the four formulations prepared. The mechanical properties of the matrixes obtained are shown in Table 4. The pH of the final mix with the maximum quantity of incineration ashes (50% incineration ashes plus cement plus water) was measured before pouring it inside the PVC tube. The value was about 13.5. The pH of the mix without ashes (cement plus water) was measured in the same way and it yielded a value of about 12.7.

The electrochemical parameters normally used to characterise the corrosion behaviour of steel in concrete were monitored periodically. These parameters included the electrical resistivity of the cemented waste-forms ( $\rho$ ) determined from resistance measurements between the steel sheet and the MMO reference electrode using a sinusoidal signal of 10 mV in amplitude at a frequency of 10 kHz; the corrosion potential ( $E_{\text{corr}}$ ) measured against the MMO reference electrode and the corrosion rate (CR)

**Table 1**  
General properties of the ion-exchange resins (provided by the manufacturers).

Name	Lewatit® monoplus S 100 KR	Lewatit® monoplus M 500 KR
Classification	Cationic strong acid	Anionic strong base
Ionic form	H <sup>+</sup>	OH <sup>-</sup>
Functional group	Sulphonic acid	Quaternary amine, type I
Matrix	Crosslinked polystyrene	Crosslinked polystyrene
Structure	Gel type beds	Gel type beds
Mean bead size (mm)	0.62 (±0.05)	0.64 (±0.05)
Density dry (g/ml)	1.22	1.08
Bulk density wet (g/L)	780	650
Exchange capacity (eq/ml)	1.8	1.0
Water retention (%)	47/53	65/75

**Table 2**  
Composition of the cement used (g/100 g).

Compound	%
SiO <sub>2</sub>	21.4
CaO	64.5
Al <sub>2</sub> O <sub>3</sub>	3.46
Fe <sub>2</sub> O <sub>3</sub>	4.90
SO <sub>3</sub>	2.04
MgO	0.82
Na <sub>2</sub> O	0.07
K <sub>2</sub> O	0.93
Cl <sup>-</sup>	<0.01
S <sup>-</sup>	<0.01
Insoluble matter	0.20
Loss after calcination	1.12

**Table 3**  
Composition of the simulated ashes (g/100 g).

Compound	%
SiO <sub>2</sub>	12.100
Al <sub>2</sub> O <sub>3</sub>	3.700
Fe <sub>2</sub> O <sub>3</sub>	4.600
CaO	12.200
MgO	6.200
TiO <sub>2</sub>	28.600
NaCl	15.660
Ca <sub>2</sub> SO <sub>4</sub>	1.596
Na <sub>3</sub> PO <sub>4</sub>	8.310
C	7.034

**Table 4**  
Mechanical properties of the different formulations used for ashes cementation.

Ash mass/total solid mass	Compressive strength (MPa)	Flexural strength (MPa)
0	43.8 ± 1.9	7.6 ± 1.3
10	38.7 ± 0.6	4.4 ± 0.8
30	22.2 ± 0.7	3.4 ± 0.7
50	8.2 ± 1.0	2.7 ± 0.5

obtained from polarisation resistance ( $R_p$ ) measurements and the application of the Stern–Geary relationship. Repeatable results were obtained in all cases, and representative values are reported in the results section. The potentials are reported in the copper/saturated copper sulphate reference electrode scale CSE ( $0.00 V_{CSE} = 0.32 V_{NHE}$ ).

**3. Results and discussion**

Fig. 2 is a scanning electron micrograph of the resins solidified in Ordinary Portland Cement. It can be seen that the resins and cement had not solidified together, with the resins physically encapsulated rather than fully bonded. Moreover, some resin particles had dropped from the cement matrix leaving holes.

Fig. 3 shows the matrix electrical resistivity as a function of time. In general, the matrix electrical resistivity had a tendency to increase with time, which reflects the continuous hydration process exhibited by the system at an early stage. The specimens containing chloride ions show lower resistivity values than those with no additions or with the addition of sulphate ions.

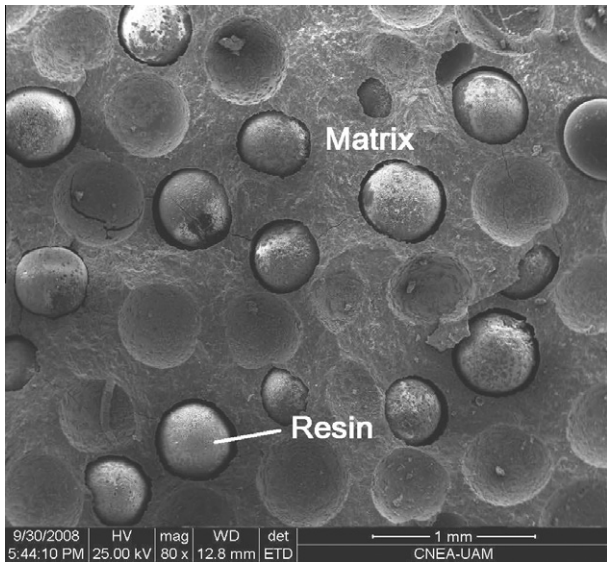


Fig. 2. Resins solidified into cement matrix.

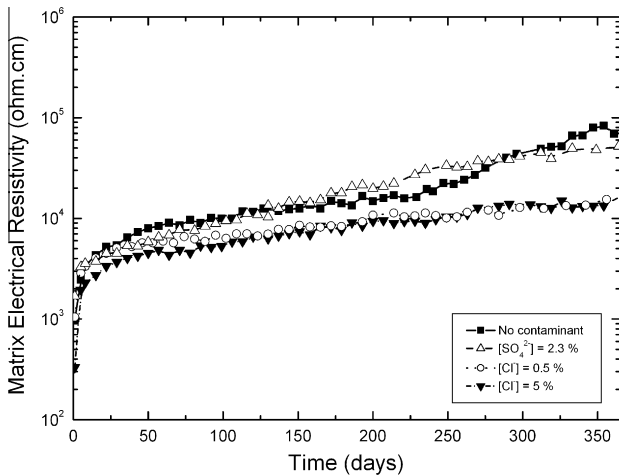


Fig. 3. Matrix electrical resistivity as a function of time for the tested formulations.

The evolution of the corrosion potential is shown in Fig. 4. When no aggressive ions were present in the mix the potential remained stable with a value close to  $-0.1 V_{CSE}$ . The same behaviour is found when sulphate ions are added. In contrast, additions of 0.5% chloride ions shift the corrosion potential towards more negative values (close to  $-0.3 V_{CSE}$ ) after an induction time of approximately 30 days. A similar behaviour is found for 5% chloride addition, but in this case the corrosion potential reaches even more negative values after shorter induction times, and reaches a mean value close to, approximately,  $-0.45 V_{CSE}$ .

Fig. 5 shows the corrosion rate of steel as a function of time. Corrosion rates 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 [18] and  $k$  is another constant that allows conversion of corrosion current density into corrosion rates. The value of  $B$  is equal to 0.026 V when the steel is in the active state and 0.052 V when the steel is in the passive state. The state of the steel is determined by its corrosion potential: according to ASTM standards [19], when the rebar potential is higher than  $-0.2 V_{CSE}$  the rebar is passive and when the potential is lower than  $-0.35 V_{CSE}$  the steel is active. In the present work when the corrosion potential is between  $-0.35$  and  $-0.2 V_{CSE}$ , a conservative approach was applied and the passive state was assumed. The value of  $k$  is derived from the application of Faraday's Law: when  $B$  is in volts and  $R_p$  in  $\Omega \text{ cm}^2$ , a value of  $k$  equal to  $11.6 \times 10^6$  yields the corrosion rate

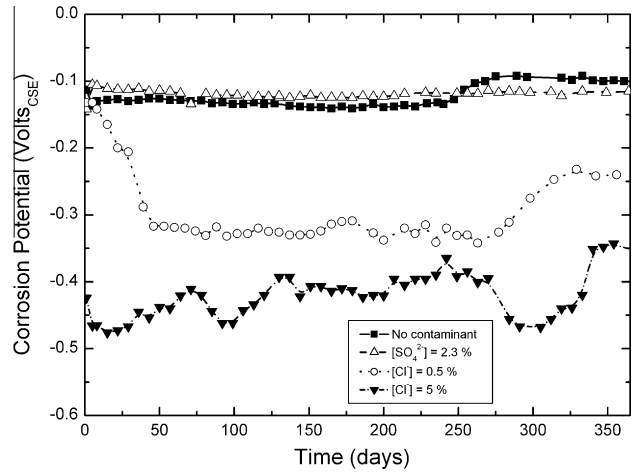


Fig. 4. Corrosion potential as a function of time for the tested formulations.

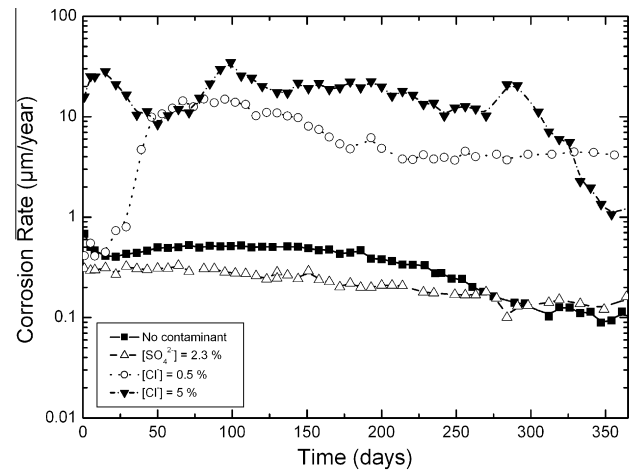


Fig. 5. Corrosion rate of steel as a function of time for the tested formulations.

in  $\mu\text{m}/\text{year}$ . Due to the high electrical resistivity of the matrix, the value of  $R_p$  was calculated taken into account the ohmic drop effect.

In agreement with the corrosion potential evolution, the CR is low ( $<1 \mu\text{m}/\text{year}$ ) for mixtures with no additions and when sulphate ions are added to the mix. On the other hand, for additions of 0.5% chloride ions, the CR increases with time during the first 50 days and then stays relatively constant at a value close to  $10 \mu\text{m}/\text{year}$ . For 5% chloride addition, the CR values are close to  $10 \mu\text{m}/\text{year}$  from the beginning of the measurements, they remain almost unchanged for most of the 1-year period, and a drop in the CR of these specimens is observed in the last days of the measurements. It can be concluded that, when the chloride content is higher than 0.5%, the CR is approximately equal to  $10 \mu\text{m}/\text{year}$ . As a consequence, for chloride contents higher than 0.5%, and assuming a drum wall thickness of 1 mm, it is expected that the drum will be perforated in no less than 100 years. As was mentioned above, and due to the conservative approach adopted, the steel drums are not considered as physical barriers in the safety analysis, as the concrete is assumed to be the sole barrier to prevent radionuclide release during the lifespan of the nuclear container. However, from the results obtained in the present work, an extra security period of 100 years is obtained. In addition, it should be mentioned that in the design of the facility it is foreseen that the drums will be internally coated with some kind of protective paint. In that case our results are very conservative but, if there is a flaw in the coating, the localized corrosion rate under paint film could be much higher than predicted in this work and this fact deserves further study.

Fig. 6 is an optical micrograph of a steel specimen in contact with cemented ion-exchange resins contaminated with 0.5% chloride after 1 year exposure time.

As for the behaviour of the steel in contact with cemented simulated ashes, the higher the ash content in the matrix, the higher the aggressiveness of the mix. After a stabilization period of about 40 days both, the corrosion potential and the corrosion rate remain almost constant over the time period of 1 year. Fig. 7 shows the corrosion potential and the corrosion rate of representative specimens after 1 year's measurements. The corrosion potential decreases and the corrosion rate increases as the ash content increases. This behaviour may be attributed to the increase in the chloride content when increasing the ash content in the matrix. As for the electrical resistivity of the matrix in these cases, it was found that the electrical resistivity had a tendency to increase with time, reflecting the continuous hydration processes occurring in

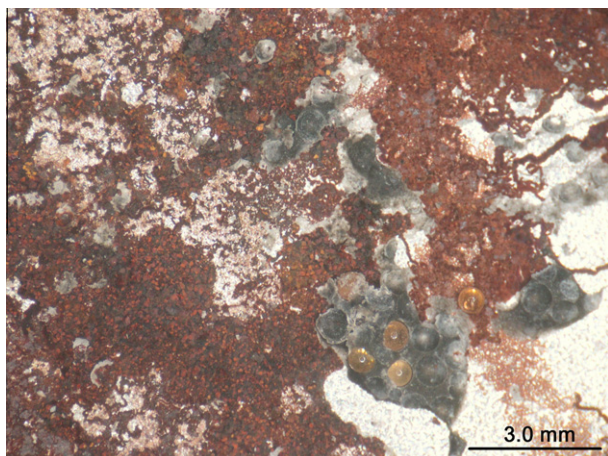


Fig. 6. Optical micrograph of a steel specimen in contact with cemented ion-exchange resins contaminated with 0.5% chloride after 1 year exposure time.

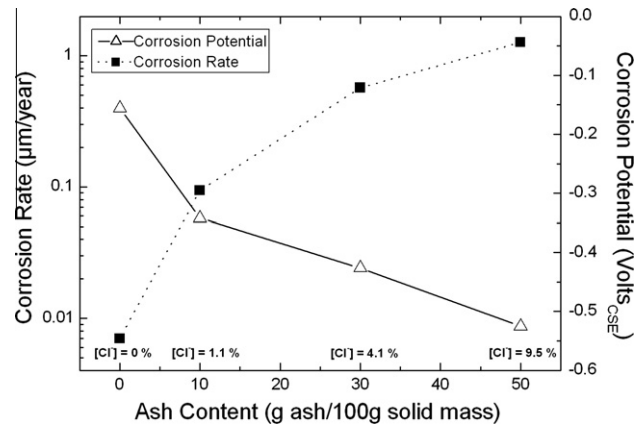


Fig. 7. Corrosion rate and corrosion potential of steel as a function of ash content. The chloride content of the matrix with respect to cement mass is also included.

the system during the early stages. The specimens containing high ash contents showed lower resistivity values than those with no additions or with the addition of little ash.

From the results obtained in the present work it can be concluded that cementation of ashes with ash contents up to 50% is possible. In this case the CR is not higher than  $1 \mu\text{m}/\text{year}$ , which yields an extra security period of 1000 years, much more than the service lifespan of the facility.

#### 4. Conclusions

- The corrosion rate of steel in contact with cemented ion-exchange resins in the absence of contaminants or in the presence of 2.3% (less than  $1 \mu\text{m}/\text{year}$ ).
- The presence of chloride ions increases the corrosion rate of steel. For chloride contents higher than 0.5% the corrosion rate reaches values close to  $10 \mu\text{m}/\text{year}$ , which implies that the drum could be perforated in about 100 years.
- The corrosion rate of the steel in contact with cemented ashes, with ash contents up to 50%, is low, yielding an extra security period much higher than the expected lifespan of the container.
- Cementation of radioactive ash poses no special risks regarding corrosion of the steel drums that contain them; corrosion of steel drums that contain cemented ion-exchange resins may be of importance if the matrix is highly contaminated with chloride ions.

#### Acknowledgements

The financial support of the CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), the ANPCYT, (Agencia Nacional de Promoción Científica y Tecnológica), and UNSAM (Universidad Nacional de San Martín), Argentina, is acknowledged.

#### References

- [1] V.M. Efrementkov, IAEA Bulletin 4 (1989) 37–42.
- [2] Application of ion-exchange processes for the treatment of radioactive waste and management of spent ion exchangers, Technical Reports Series No 408, International Atomic Energy Agency, Vienna, 2002.
- [3] F.P. Glasser, Cem. Concr. Res. 22 (1992) 201–216.
- [4] J.D. Palmer, G.A. Fairhall, Cem. Concr. Res. 22 (1992) 325–330.
- [5] M.L.D. Gougar, B.E. Scheetz, D.M. Roy, Waste Manage. 16 (1996) 295–303.
- [6] J.M. Ducoulombier, B. Lantes, M. Bordier, Nucl. Eng. Des. 176 (1997) 27–34.
- [7] P. Le Bescop, P. Bouniol, M. Jorda, Mat. Res. Symp. Proc. 176 (1990) 183–189.
- [8] I. Plecas, R. Pavlovic, S. Pavlovic, J. Nucl. Mater. 327 (2004) 171–174.
- [9] L. Junfeng, Z. Gang, W. Jianlong, Nucl. Eng. Des. 235 (2005) 817–820.
- [10] L. Junfeng, W. Jianlong, J. Hazard. Mater. B 135 (2006) 443–448.

- [11] X. Gan, M. Lin, L. Bao, Y. Zhang, Z. Zhang, *J. Nucl. Sci. Technol.* 45 (2008) 1084–1090.
- [12] Characterization of simulated radioactive waste ashes and evaluation of conditioning methods (in Spanish), Technical Report IP/IQ-001-262/89, Departamento de Ingeniería Química y Ambiental, Escuela Superior de Ingenieros Industriales de Sevilla, Sevilla, 1991.
- [13] F. Frizon, C. Cau-dit-Caumes, *J. Nucl. Mater.* 359 (2006) 162–173.
- [14] U. Angst, B. Elsener, C.K. Larsen, Ø. Vennesland, *Cem. Concr. Res.* 39 (2009) 1122–1138.
- [15] A.D. Keitelman, J.R. Galvele, *Corr. Sci.* 22 (1982) 739–751.
- [16] G.S. Duffó, S.B. Farina, C.M. Giordano, *Electrochim. Acta* 54 (2009) 1010–1020.
- [17] ASTM C 305-99, Standard method of test for mechanical mixing of hydraulic cement pastes and mortars of plastic consistency, American Society of Testing and Materials, West Conshohocken, PA, USA, 1999.
- [18] C. Andrade, J.A. González, *Werkst. Korros.* 29 (1978) 515–519.
- [19] ASTM C 876-99, Standard test method for half-cell potentials of uncoated reinforcing steel in concrete, American Society of Testing and Materials, West Conshohocken, PA, USA, 1999.