

Preliminary results of corrosion monitoring studies of carbon steel overpack exposed to supercontainer concrete buffer

B. Kursten^{*1}, F. Druyts¹, L. Areias², Y. van Ingelgem³, D. De Wilde³, G. Nieubourg³, G. S. Duffó⁴ and C. Bataillon⁵

The supercontainer (SC) is the reference concept for the postconditioning of vitrified high level radioactive waste and spent fuel in Belgium. It is designed with a concrete buffer completely surrounding a carbon steel overpack. A half-scale (HST-2) experiment was set up to measure the instantaneous uniform corrosion rate, representative of the initial oxic phase, *in situ*. The test set-up has the same diameter as a full size SC, but it is limited in height to approximately half of a real SC. The corrosion rate of carbon steel is measured in four ways: weight loss measurements (carbon steel coupons), corrosion sensor based on linear polarisation resistance, corrosion sensor based on multisine electrochemical impedance spectroscopy and corrosion sensor based on single sine electrochemical impedance spectroscopy coupled to a unique analytical method. This paper presents the preliminary results of the corrosion rates measured with these independent methods.

Keywords: Uniform, Corrosion, Passive, Concrete, Steel, LPR, EIS, Disposal

This paper is part of a special issue on 'Long-Term Prediction of Corrosion Damage in Nuclear Waste Systems'

Introduction

The supercontainer (SC) is the Belgian reference concept proposed by ONDRAF/NIRAS for the packaging of vitrified high level radioactive waste (VHLW) and spent fuel (SF).^{1,2} It consists essentially of a prefabricated massive cylindrical concrete block (ordinary Portland cement), named 'the buffer', into which a watertight cylindrical carbon steel container, the so called overpack, holding either VHLW waste canisters or SF assemblies, will be inserted. There is also an alternative design option in which the concrete block will be fitted into an outer stainless steel container, termed the 'envelope'.

The reference material to construct the overpack is currently the P355 QL2 grade carbon steel. The long term safety function of the overpack is to contain the radionuclides during the thermal phase, which will last several thousands of years. The concrete buffer has a thickness of 54–70 cm (depending on the waste to be placed in the SC) and completely surrounds the over-

pack. One of the main long term functions of the concrete buffer is to provide a highly alkaline chemical environment, in which a thin but tightly adhering oxide film is formed on the surface of the carbon steel overpack that protects the underlying metal and is believed to result in very low and almost negligible uniform corrosion rates (passive dissolution). Apart from creating a favourable environment around the overpack, the concrete buffer also provides the required radiological shielding.

Half-scale prototype test

As part of the present experimental programme to verify the feasibility of constructing the SC, a second half-scale experiment (HST-2) was performed in 2013. The test set-up has the same diameter as a full size SC (~2.1 m), but it is limited in height (~3.5 m) to approximately half that of a real SC. Figure 1 shows the general set-up of the half-scale test.

The outer mould consists of two cylindrical steel segments held together and to a steel base plate by means of bolts. A steel inner mould is inserted to create an inner cavity for later installation of the heater. The space between the outer and inner mould is filled with a non-reinforced, self-compacting concrete (i.e. the buffer). After removal of the inner mould, a carbon steel container with a diameter of 508 mm and a thickness of 15.06 mm, simulating the overpack, is inserted in the remaining cavity. Inside the overpack are four heating elements to simulate the heat generated by the

¹SCK-CEN, Boeretang 200, 2400 Mol, Belgium

²EIG EURIDICE, c/o SCK-CEN, Boeretang 200, Mol 2400, Belgium

³Vrije Universiteit Brussel, VUB, SURF, Pleinlaan 2, Brussel 1050, Belgium

⁴Comisión Nacional de Energía Atómica, CNEA-CONICET-UNSAM, Corrosion Department, Av. Gral. Paz 1499, (1650KNA) Buenos Aires, Argentina

⁵CEA, DEN, DPC, SCCME, Laboratoire d'Etude de la Corrosion Aqueuse, Gif-sur-Yvette F-91191, France

*Corresponding author, email bkursten@sckcen.be



a one of two steel cylindrical segments of outer mould ($\varnothing \sim 2.1$ m; height ~ 3.5 m); b inner steel tapered mould ($\varnothing \sim 0.5$ m); c assembled mould before casting of concrete buffer; d cured concrete buffer during installation of heater

1 Set-up of half-scale test

radioactive waste in a real overpack containing two high level waste canisters. The simulated overpack is filled with fine grained, clean sand to help create a homogeneous heat distribution inside the overpack. The gap between the concrete buffer and the carbon steel overpack, as well as the free space above the overpack, is filled with a self-compacting mortar (i.e. the filler).

The buffer and the filler have essentially the same material composition, which consists of ordinary Portland cement and limestone aggregates. However, the filler is a mortar with a higher water/cement ratio and finer aggregates than the buffer. The composition of both the buffer and the filler, as well as some of its properties, is summarised in Table 1. The concrete buffer and filler are fabricated according to a precise procedure: the various aggregates (0/4–2/6–6/14 mm) are first mixed for 30 s; the cement and limestone filler are then added and mixed for 60 s; subsequently, water is added and mixed for 120 s; and finally, a stabiliser (VMA Rheomatrix) and a super-plasticiser (Glenium) are added to the concrete mix and mixed for an additional 180 s.

Set-up of corrosion experiments

An experimental investigation was initiated to get a better insight into the corrosion behaviour of the carbon steel overpack when exposed to the high pH concrete buffer of the SC, which is representative of the initial 'oxic' phase of the disposal period. Four different techniques were used to measure the *in situ* uniform corrosion rate of P355 QL2 grade carbon steel in the HST-2 prototype:

- (i) weight loss measurements
- (ii) a corrosion sensor developed at the Argentine National Atomic Energy Commission (CNEA), based on the linear polarisation resistance (LPR) technique
- (iii) a corrosion sensor developed at the French Alternative Energies and Atomic Energy Commission (CEA), based on the single sine electrochemical impedance spectroscopy (EIS) method

- (iv) a corrosion sensor (PermaZEN) developed within the SURF Research Group of the Free University of Brussels (VUB), based on the multisine EIS method.

The weight loss coupons and corrosion sensors were attached to a steel wire that was fixed between a bottom plate installed at the bottom of the mould and a temporary bridge placed across the top of the outer mould. The steel wire was Teflon lined to electrically isolate the coupons and sensors from the support wire and the test structure (Fig. 2).

Weight loss coupons

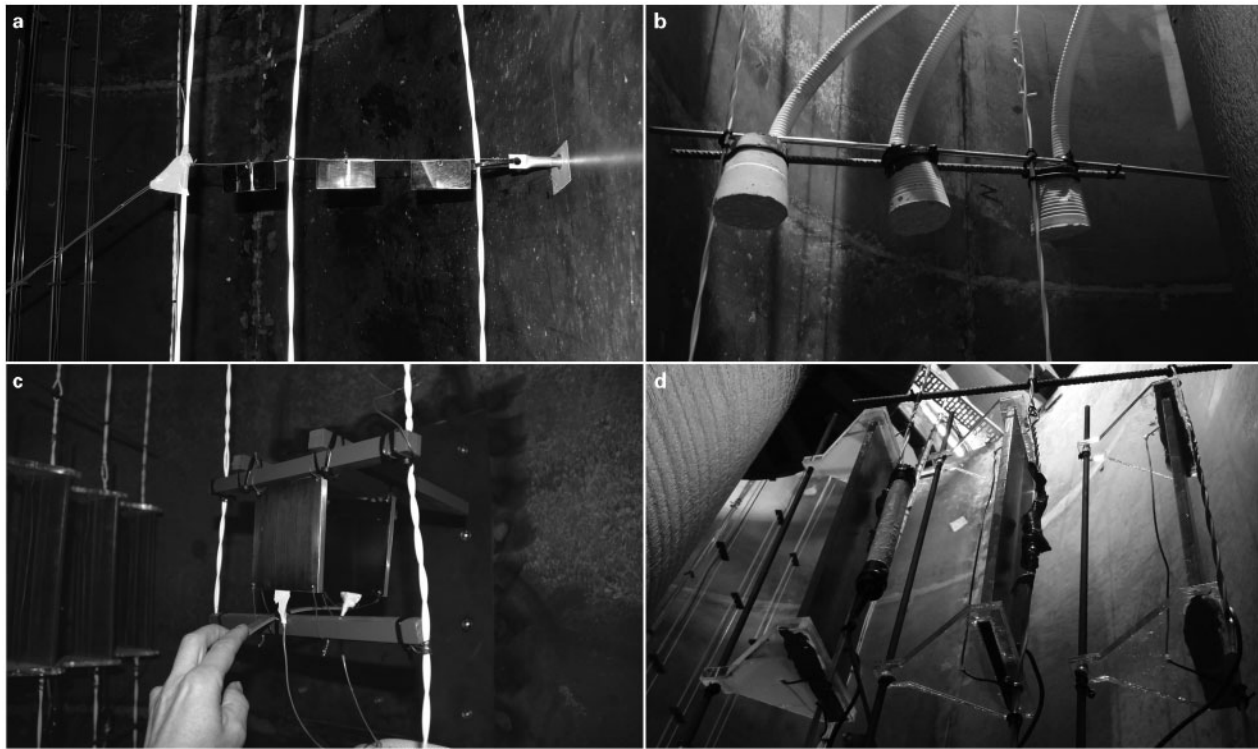
The weight loss coupons ($60 \times 30 \times 3$ mm) were machined from a 3 cm thick plate having the same specifications as the reference carbon steel for the SC (i.e. P355 QL2 grade C steel). The surface of the coupons was polished to a P4000 SiC paper finish. In total, six carbon steel coupons were cast into the concrete buffer of the HST-2 prototype at $\sim 1/4$ height (860–875 mm) and radially at three distances from the outer steel mould (15–25–35 cm) (Fig. 2a).

At the end of the experiment, the coupons will be retrieved by overcoring using a coring bit slightly larger

Table 1 Composition of self-compacting concrete (buffer) and mortar (filler) used in HST-2³

Composition	Buffer*	Filler*
Cement CEM I 42.5	350.00	235.00
LH LA HSR/kg m ⁻³		
Calcitec 2001 M (limestone)/kg m ⁻³	100.00	400.00
Limestone 0/4/kg m ⁻³	840.00	1350.00
Limestone 2/6/kg m ⁻³	327.00	...
Limestone 6/14/kg m ⁻³	559.00	...
VMA Rheomatrix 100/kg m ⁻³	0.17	...
Superplast Glenium 27/20/kg m ⁻³	8.00	3.50
Water/kg m ⁻³	175.00	235.00
Water/cement ratio	0.50	1.00
Compressive strength, 28 days/MPa	62 ± 0.7	26 ± 0.4
Flexural tensile strength, 28 days/MPa	4.7 ± 0.2	5.0 ± 0.2
Splitting tensile strength, 28 days/MPa	3.9 ± 0.1	3.9 ± 0.1
Density/kg m ⁻³	2384	2230

*The amounts shown are for dry materials.



a weight loss coupons (60 × 30 × 3 mm); b CNEA corrosion sensors; c CEA corrosion sensor; d VUB PermaZEN corrosion sensors
2 Photographs of different corrosion test set-ups in HST-2 prototype mould before casting of concrete buffer

than the coupons. Afterwards, the concrete will be removed mechanically, the coupons will be chemically cleaned and mass losses will be measured. These coupons will serve to calculate an ‘average’ uniform corrosion rate over the entire exposure period and to study the thickness and the composition of the oxide film that has formed on the surface of the coupons.

Argentine National Atomic Energy Commission corrosion sensors

The CNEA corrosion sensor is able to measure simultaneously the instantaneous uniform corrosion rate, the open circuit potential, the temperature inside the concrete, the electrical concrete resistivity, the oxygen flow in the concrete and the chloride concentration in the concrete.⁴

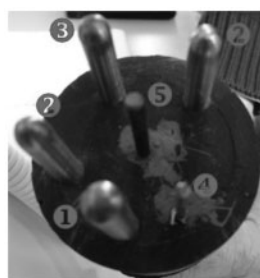
The corrosion sensor contains one carbon steel rod (working electrode), two stainless steel rods (counter electrode), a mixed metal oxide (MMO) reference electrode, a Ag/AgCl electrode and a Pt 100 type thermometer, all of them embedded in a special epoxy resin that is resistant to the high alkaline environment of the concrete. The working electrode consisted of a cylindrical rod ($\varnothing=6$ mm;

$L=70$ mm) machined from a 3 cm thick plate of the reference carbon steel grade P355 QL2. The stainless steel counter electrode rods had the same dimensions as the carbon steel working electrode rod. A close-up of the CNEA corrosion sensor is shown in Fig. 3. A detailed description of the sensor is given elsewhere.⁴

Corrosion rates were measured using the LPR method.⁴ The procedure involves first measuring the open circuit potential E_{CORR} of the carbon steel rod against the MMO reference electrode. The carbon steel working electrode is then cathodically polarised at a preselected current density I_{APPL} , generally in the range of 10^{-7} – 10^{-6} A cm⁻², using the two stainless steel rods as counter electrode. The resulting potential E of the carbon steel rod is measured against the MMO reference electrode after a certain period of time (~ 1 min). The polarisation resistance R_p is thus obtained as

$$R_p = - \frac{E - E_{CORR}}{I_{APPL}} - R_s \quad (1)$$

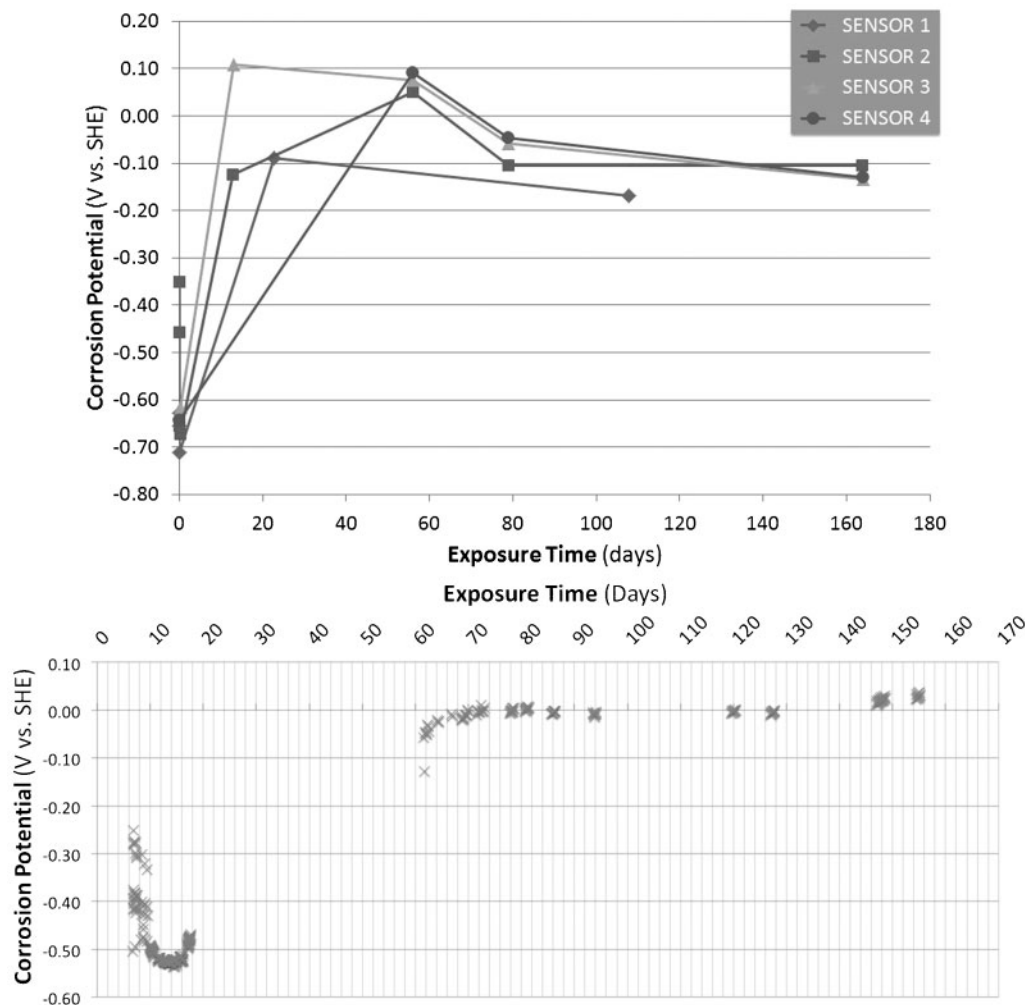
where R_s is the concrete resistance (as measured with the same sensor) between the carbon steel rod and



- 1 Pt 100 type thermometer
- 2 two stainless steel rods (counter electrode; $\varnothing = 6$ mm)
- 3 one carbon steel rod (working electrode; $\varnothing = 6$ mm)
- 4 Ag/AgCl electrode
- 5 mixed-metal oxide (MMO) reference electrode



3 Corrosion sensor developed at CNEA: different components of sensor (left); sensor conditioned and ready for installation in HST-2 test (right)



4 Evolution of corrosion potential measured with CNEA sensor (top) and VUB PermZEN sensor (bottom) with respect to SHE

the MMO reference electrode. The corrosion rate is calculated with the following equation

$$I_{CORR} = \frac{B}{R_p} \tag{2}$$

where *B* is a proportionality constant whose value is chosen to be 0.026 or 0.052 V, for the cases where the steel is in the active or passive corrosion state respectively.⁵

In total, four CNEA corrosion sensors were installed in the HST-2 prototype: three at ~1/3 height (1300 mm) positioned radially at three distances from the outer steel mould (13–26–43 cm) (Fig. 2*b*), and one at the top in the filler. Before installing the sensors in the HST-2 prototype, the exposed part of the electrodes was covered with a mortar in order to avoid the formation of air pockets close to the electrodes. A porous mortar, using only small size aggregates (0–4 mm), was used in order to develop a quick equilibrium between the sensor and the environment in the whole structure after casting the concrete buffer.⁴

Atomic Energy Commission corrosion sensors

One CEA corrosion sensor was installed in the HST-2 prototype at ~1/2 height (1730 mm) and at the mid-point between the inner and outer steel mould (Fig. 2*c*). The sensor consisted of two P355 QL2 grade carbon steel plates (100 × 100 × 4 mm) that were polished on

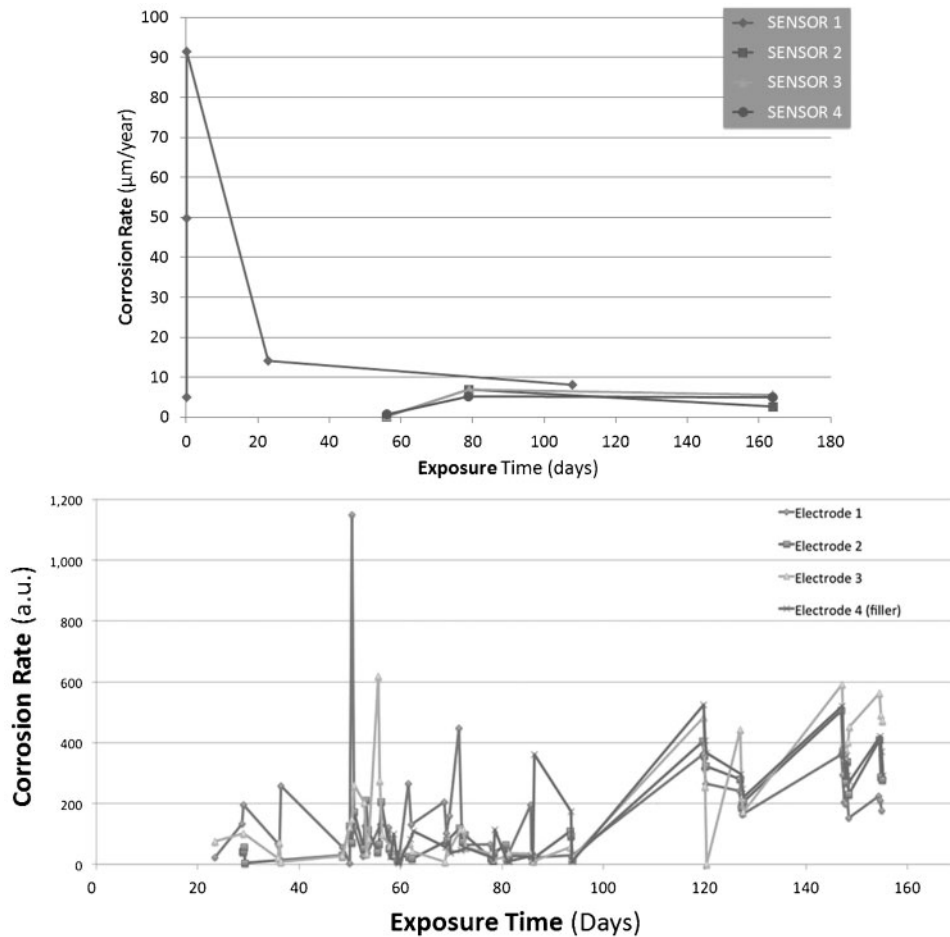
one side to a P4000 SiC paper finish. The steel plates were positioned vertically and in parallel at a distance of ~10 cm, with the polished sides facing each other.

The instantaneous uniform corrosion rate is measured using the single sine EIS method. In this technique, the steel sample is perturbed from its equilibrium by only a very small amount ($\Delta\eta$, ~10 mV). A low amplitude repeating potential wave (ac signal), of varying frequency, is imposed on top of the corrosion potential (dc signal). The resulting current response (ac signal) is then measured. The system’s impedance is calculated by analysing the response signal at each frequency. The impedance is defined as the frequency dependent, complex valued proportionality factor, $\Delta E/\Delta I$, between the applied potential and the response current.

The corrosion current density is given by the following equation

$$I_{CORR} = \frac{1}{\alpha_a n_a + \alpha_c n_c} \frac{R_T}{F} \frac{1}{R_T} \tag{3}$$

where n_a and n_c are the number of electrons exchanged in the anodic and cathodic reactions respectively, α_a and α_c are the anodic and cathode Butler–Volmer coefficients, F is the Faraday constant and R is the molar gas constant. From equation (3), it can be seen that the corrosion current density, which is directly related to the corrosion rate, is inversely proportional to the transfer resistance, R_T .



5 Evolution of instantaneous corrosion rate measured with CNEA sensor (top) and VUB PermaZEN sensor (bottom)

Bataillon (CEA) developed a unique in house analytical method to extrapolate the transfer resistance R_T from the measured impedance spectra.⁶ In short, the method consists of the following sequences:

- (i) extraction of the appropriate experimental data and converting them into the correct format
- (ii) evaluation of the electrolyte resistance R_S
- (iii) determination of the parameters of the constant phase element at low frequencies
- (iv) evaluation of the transfer resistance R_T .

Free University of Brussels PermaZEN corrosion sensors

Four PermaZEN corrosion sensors were installed in the HST-2 prototype: three at $\sim 1/2$ height (1700 mm) positioned radially at three distances from the outer steel mould (13–25–40 cm) (Fig. 2d), and one at the top in the filler. The sensor consists of a carbon steel plate (working electrode) and an MMO auxiliary electrode. The working electrode ($300 \times 85 \times 8$ mm) was machined from a 3 cm thick plate of the reference carbon steel grade P355 QL2. The working electrodes and the MMO electrodes were fixed at a distance of ~ 10 cm apart. Additionally, one commercially available Ag/AgCl reference electrode (specially designed to resist the high alkalinity of the concrete buffer) was installed in the vicinity of one of the carbon steel plates in order to monitor its open circuit potential over time. The Ag/AgCl reference electrode that was used in this study was manufactured by Borin Manufacturing, model Stelth 2.

Electrical connection to the data acquisition equipment was made using a 7 mm diameter shielded cable. The measuring sequence was performed remotely and continuously using the internet.

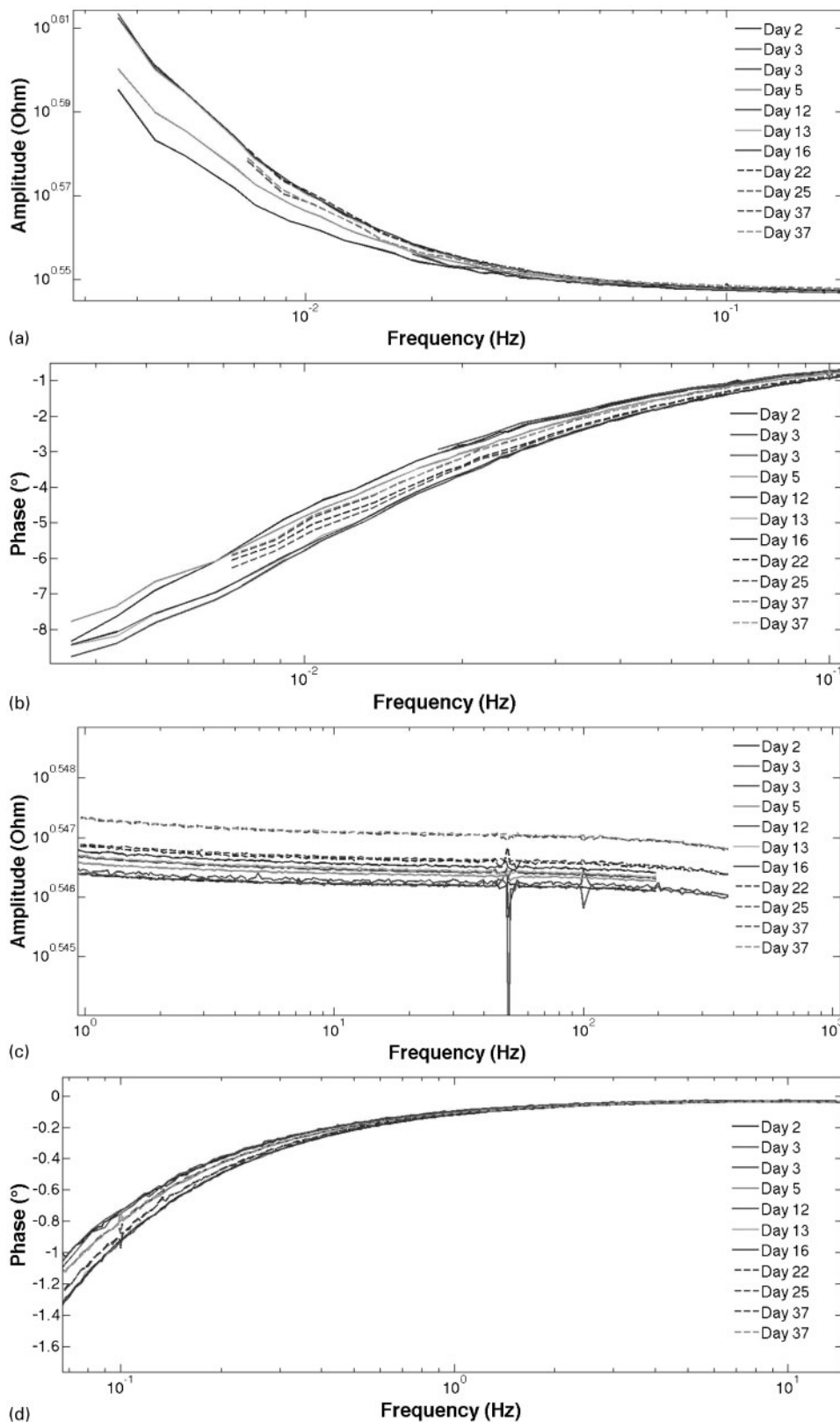
The measurement of the corrosion rate with the PermaZEN corrosion sensor is based on the multisine EIS method, which involves applying a low amplitude, multifrequency ac signal between the carbon steel plate and the MMO auxiliary electrode. The recorded response to this excitation is then analysed and interpreted using an algorithm, and the equivalent corrosion rate is then calculated. A more detailed description of the multisine EIS method is given elsewhere.^{7,8}

The PermaZEN corrosion sensor was first tested in a laboratory scale test set-up to assess its potential for measuring instantaneous corrosion rates of carbon steel exposed to a large scale concrete buffer (SC). The results of these tests were positive and confirmed the suitability of the sensors to monitor corrosion in the HST-2 prototype.⁹

Results and discussion

Figure 4 shows the evolution of the corrosion potential measured with the CNEA sensor and the VUB PermaZEN sensor. The measured potentials are given against the standard hydrogen electrode (SHE) scale. Owing to a malfunction of the VUB PermaZEN sensor, no data were recorded in the exposure period between 18 and 60 days.

In both cases, the corrosion potential showed a similar evolution over time: an initial drop immediately after casting occurred, followed by a rise and



a amplitude, low frequency domain; b phase angle, high frequency domain; c amplitude, low frequency domain; d phase angle, high frequency domain

6 Bode plots of P355 QL2 grade carbon steel embedded in SC concrete buffer

stabilisation in the range between -100 and 0 mV(SHE) after ~ 80 days of curing. This ennoblement of the corrosion potential is attributed to the formation of the passive film. The CNEA sensor installed in the filler (sensor no. 1) exhibited slightly more negative potentials

$[\sim -170$ mV(SHE)]. The more positive values were measured with the VUB PermaZEN sensor.

Figure 5 shows the evolution of the instantaneous corrosion rate measured with the CNEA sensor and the VUB PermaZEN sensor. Owing to a malfunction of

three of the CNEA sensors, no measurements were made with them for the first 56 days of the test. The corrosion activity measured with the VUB PermaZEN sensor is given in an arbitrary unit. Studies to correlate the measured 'arbitrary' unit to a 'real' corrosion rate expressed in $\mu\text{m year}^{-1}$ are currently ongoing.

The CNEA sensor revealed a very high increase in the corrosion rate in the first hours after casting of the concrete, reaching a value of $\sim 90 \mu\text{m/year}$. This increase is attributed to the formation of the passive film. After formation and stabilisation of the passive film, the corrosion rate decreased rapidly to relatively low values. The measured corrosion rate after ~ 160 days of exposure was of the order of $4\text{--}5 \mu\text{m/year}$.

The VUB PermaZEN sensor showed an initial slow decrease in the corrosion activity, followed by a sudden increase after ~ 90 days. The reason for this increase is still not fully understood. Interference between the measuring device and the installed electrical heater could be a potential source of noise pickup (heating was started 2 months after casting of the concrete). Studies to separate the contributions of the electrical (heater) and electrochemical (corrosion processes) signals are ongoing to try to clarify this. Another reason could be a loss of contact between the embedded electrodes and the surrounding concrete due to volume changes in the concrete.

The EIS measurements enable a distinction to be made between low frequency effects, due to the formation and stabilisation of the passivation layer, and high frequency effects attributed to the bulk properties of the concrete. The changes in amplitude and phase angle as a function of frequency calculated for the PermaZEN sensors provide additional information on the characteristics of the passive film. These results are shown in Fig. 6.

The results show an increase in amplitude with time for frequencies below ~ 0.1 Hz (Fig. 6a), during the first 12 days after casting, indicating a decrease in corrosion activity and confirming measurements presented earlier for corrosion potential and corrosion rate. After 12 days, the amplitudes converged and remained approximately constant with time. Above 0.1 Hz (Fig. 6b), the amplitude continuously increased with time. This increase is believed to be due to a decrease in the concrete's conductivity with time caused by the progressive 'drying out' of the concrete buffer.

For frequencies below ~ 0.1 Hz (Fig. 6c), the phase shift decreased with time in the initial 16 days, reflecting the effect of capacitive changes due to the presence of the double layer. From day 16 on, the phase value at lower frequencies increases again as further changes in the composition due to the hydration reactions may further change the response of the double layer. At higher frequencies (Fig. 6d), the phase shift converged to zero, indicating the dominance of the resistive behaviour of the electrolyte.

Conclusions

The measurements obtained with the different corrosion sensors embedded in the concrete buffer of the HST-2 prototype provided an insight into the behaviour of the P355 QL2 grade carbon steel overpack when exposed to the high pH of the concrete buffer. Since the test was performed in air, the results presented here represent the initial oxidic phase expected during the first period of disposal in an underground disposal facility.

The main aim of the corrosion monitoring campaign was to obtain uniform corrosion rates using four independent methods: weight loss measurements, LPR technique, single sine EIS method and multisine EIS method. In total, six weight loss coupons, four CNEA corrosion sensors, four VUB PermaZEN corrosion sensors and one CEA corrosion sensor were embedded in the HST-2 prototype.

The corrosion potential increased to values in the range between -100 and 0 mV(SHE) after ~ 80 days of curing. This ennoblement of the corrosion potential is attributed to the formation of a passive film.

The corrosion rate showed a steep rise during the first hours after casting to a value of $\sim 90 \mu\text{m/year}$. This increase was attributed to the formation of the passive film. After ~ 160 days of exposure, the corrosion rate decreased to $\sim 4\text{--}5 \mu\text{m/year}$.

The impedance measurements confirmed the decrease in corrosion activity with time. The data measured with the CEA corrosion sensor still need to be further analysed.

Finally, an area that needs further development concerns the automation of the measurement procedure for the CNEA and CEA sensors. The procedure could be made similar to the one used by the PermaZEN sensors, which can be operated fully automatically and provide continuous measurements via a remote internet connection.

Acknowledgements

The work presented in this paper was undertaken in cooperation and with the financial support of the Belgian Agency for Radioactive Waste and Fissile Materials (ONDRAF/NIRAS). The authors gratefully acknowledge the Argentine National Atomic Energy Commission (CNEA) for providing corrosion sensors and the French National Radioactive Waste Management Agency (Andra) for their guidance in installing the corrosion sensors.

References

1. 'The long-term safety strategy for the geological disposal of radioactive waste', Report no. NIRON-TR 2009-14 E, Belgian Agency for Radioactive Waste and Fissile Materials (ONDRAF/NIRAS), Brussels, Belgium, 2009.
2. 'Feasibility strategy and feasibility assessment methodology for the geological disposal of radioactive waste', Report no. NIRON-TR 2010-19 E, Belgian Agency for Radioactive Waste and Fissile Materials (ONDRAF/NIRAS), Brussels, Belgium, 2010.
3. B. Craeye: '2nd half-scale test for validation of the early-age thermo-mechanical behaviour of the supercontainer: obtained concrete properties', Technical report no. OR 228, Betonadvies Gijko, Temse, Belgium, 2013.
4. G. S. Duffö and S. B. Farina: *Constr. Build. Mater.*, 2009, **23**, 2746–2751.
5. C. Andrade and J. A. González: *Werkst. Korros.*, 1978, **29**, 515–519.
6. C. Bataillon: 'Suivi corrosimétrique des aciers faiblement alliés en laboratoires souterrains', Report no. RT DPC/SCCME 11-847-A, Commissariat à l'énergie atomique et aux énergies alternatives (CEA), France, 2011.
7. E. van Gheem, R. Pintelon, J. Vereecken, J. Schoukens, A. Hubin, P. Verboven and O. Blajiev: *Electrochim. Acta*, 2004, **49**, (26), 4753–4762.
8. T. Breugelmanns, J. Lataire, T. Muselle, E. Tourwé, R. Pintelon and A. Hubin: *Electrochim. Acta*, 2012, **76**, 375–382.
9. B. Kursten, L. Areias, F. Druyts, R. Gens, P. van Marcke, J. Verstricht, L. Villers, A. van Cotthem, D. De Wilde and Y. van Ingelgem: 'Reduced scale tests to assess corrosion of a steel overpack in the Belgian Supercontainer', Proc. MoDeRn International Repository on 'Monitoring in Geological Disposal of Radioactive Waste' - Conf. and Workshop, Luxembourg, 19–21, March 2013, MoDeRN EURATOM consortium and the European Commission, S6T07.