Lessons learned from *in situ* corrosion experiments in the HADES URL



Bruno Kursten^{1*}, Sébastien Caes¹, Valdir de Souza¹ and Roberto Gaggiano²

¹SCK CEN, Belgian Nuclear Research Centre, Institute for Environment, Health and Safety, Boeretang 200, B-2400 Mol, Belgium

²ONDRAF/NIRAS, Kunstlaan 14, B-1210 Brussels, Belgium

D BK, 0000-0002-6408-9476

*Correspondence: bruno.kursten@sckcen.be

Abstract: A wide range of metals have been studied as a candidate container material to be considered in the geological disposal concept of high-level radioactive waste and spent fuel in Belgium. More than 40 years ago, SCK CEN started studies on the corrosion of these metals. The HADES underground research laboratory (URL) played an important role in the corrosion research as it enabled *in situ* corrosion experiments to be carried out that simulate realistic disposal conditions as closely as possible. These experiments consisted of placing metallic coupons on a steel support tube, heated from the inside, that was installed in Boom Clay, thereby exposing the coupons to various conditions representative of the disposal concept that was considered at that time. Test durations lasted from 6 months to approximately 7.5 years. This paper summarizes the results from the various corrosion studies and discusses their implications in the choice of disposal concept. One of the main outcomes of these experiments was a change of rationale regarding the choice of the container material from carbon steel (corrosion-allowance) to stainless steel (corrosion-resistant). The main arguments for this change were the need to avoid severe pitting corrosion during the aerobic period and to minimize the generation of hydrogen gas during the subsequent anaerobic period.

Geological disposal is internationally accepted as the most appropriate long-term management solution for high-level and long-lived radioactive waste. This means that the waste is placed in a deep geological repository (DGR). The safety of geological disposal relies on the multibarrier concept: a combination of engineered (man-made) barriers and a natural barrier (i.e. the host rock formation). In this concept, the metallic container that encloses the radioactive waste packages is one of the main engineered barriers. It can contribute to containing the radionuclides and other contaminants so that they are not released into the biosphere in concentrations that could pose an unacceptable risk for man and the environment.

The main threat to container integrity is corrosion through contact with the groundwater present in the host rock. In Belgium, the metallic container needs to be designed so that it remains intact and provides complete containment of the heat-generating waste during the thermal phase. The thermal phase is the phase during which the host rock is at an elevated temperature (i.e. higher than 25°C) due to the heat generated by the high-level waste (HLW) or spent fuel (SF). This phase is assumed to last for several hundred years for vitrified HLW and possibly up to a few thousand years for SF. Ensuring that no radionuclides are released during this phase avoids the need to assess the complex radionuclide migration through the host rock at elevated temperatures (NEA 2008; Chapman and Hooper 2012).

The technical solution recommended by the Belgian radioactive waste management organization ONDRAF/NIRAS for the long-term management of HLW and SF is geological disposal in poorly indurated clay (ONDRAF/NIRAS 2013). Boom Clay has been studied for many years as the reference host formation for this purpose. It is located in the NE of Belgium, has a thickness of about 100 m, and extends underneath the Mol-Dessel nuclear research site at a depth between 190 and 290 m. It mainly consists of clay minerals (25-71 wt%), siliciclastics (27-72 wt%, mainly quartz and feldspars), carbonates (0-4 wt%), pyrite (0.5-3 wt%) and organic carbon (0.5-3.5 wt%) (Zeelmaekers et al. 2015). It has favourable properties, such as a low hydraulic conductivity, a high sorption capacity for many radionuclides and self-healing properties because of its elasto-plastic behaviour (Maes et al. 2004: Bastiaens et al. 2007: Van Geet et al. 2008; Yu et al. 2013). All of these properties help to retard the migration of radionuclides after their release from the engineered barrier system (EBS) into the host rock. In the Boom Clay, radionuclide migration is dominated by diffusion. Advection plays a secondary role due to the clay's very low

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Fig. 1. Drawing of a supercontainer containing (a) two vitrified high-level waste canisters and (b) four spent fuel assemblies (ONDRAF/NIRAS 2019). SNFA, spent nuclear fuel assembly.

hydraulic conductivity and the absence of preferential pathways for water (such as large fractures) (Neerdael and Volckaert 2001).

The design that is currently (since c. 2004) considered as the reference design for the geological disposal of vitrified HLW and SF in Belgium is the so-called supercontainer concept (Fig. 1). The details of this design are given in another paper included in this special publication (Li et al. 2023). The supercontainer consists of placing vitrified HLW canisters or SF assemblies in a carbon steel overpack. This overpack is surrounded by a concrete buffer made of ordinary Portland cement (OPC). The cavity between the overpack and the concrete buffer is filled with a cementitious material (i.e. the filler). In the presently preferred design option, the buffer is surrounded by a stainless steel casing (i.e. the envelope). These supercontainers are placed in concrete-lined disposal galleries. The void space between the gallery lining and the supercontainer is also backfilled with a cement-based material (ONDRAF/NIRAS 2013, 2019).

However, the disposal concept and the repository design have evolved quite a lot over the past 40–50 years (Fig. 2). This has greatly affected the experimental approach adopted for the corrosion studies. The *in situ* corrosion experiments presented in this paper were conceived based on the SAFIR-2 design (Fig. 3). This design was developed in the late 1980s and remained the reference design until



Fig. 2. Schematic representation of the evolution of the disposal concepts and repository designs over time. OPC, ordinary Portland cement.



Fig. 3. Schematic view of (**a**) the repository architecture and (**b**) the disposal concept according to the SAFIR-2 reference design (before 2004) (Mallants *et al.* 2001; Neerdael and Volckaert 2001).

about 2004. In this design, the layout of the DGR consisted of a horizontal network of rectilinear disposal galleries ($\emptyset_{int} = 2 \text{ m}$) constructed in the mid-plane of the Boom Clay Formation. The disposal galleries could be as long as 800 m. Two main galleries ($Ø_{int}$ = 3.5 m) connected the disposal galleries to two vertical access shafts ($\emptyset_{int} \approx 6$ m). The access shafts and the disposal galleries would be lined with concrete segments in order to ensure the mechanical stability during the operational phase of the repository. In the centre of the disposal gallery, a stainless steel disposal tube ($\emptyset_{int} = 0.55$ m, wall thickness c. 10 mm) would be installed. Pre-compacted clay-based backfill blocks would fill the gap between the central disposal tube and the gallery lining. The primary waste packages (either vitrified HLW canisters or SF assemblies) would be enclosed in a 30 mm-thick individual stainless steel overpack, which in turn would be pushed into the stainless steel disposal tube using an automated system (pusher robot)

(Neerdael and Volckaert 2001; ONDRAF/NIRAS 2001; Kursten and Druyts 2006).

In the current supercontainer concept, the carbon steel overpack will come into contact with OPC concrete porewater, which has a very high pH of c. 13.5 at 25°C. Experience has shown that when carbon steel is exposed to such a highly alkaline environment, a thin but tightly adhering oxide film is formed on the surface of carbon steel. This will passivate the steel, leading to passive current densities that can correspond to corrosion rates as low as only a few nanometers per year (under anoxic conditions and in the absence of any aggressive species) (He et al. 2017; Senior et al. 2017, 2021; Smart et al. 2017, 2021; Kursten et al. 2021). This passivation and the potentially low corrosion rates are some of the main reasons for choosing carbon steel as the reference overpack material and OPC-based concrete as the reference buffer material. However, in the SAFIR-2 concept, which is relevant to the in situ

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experiments described in this paper, the metallic overpack, fabricated from stainless steel, would be exposed to bentonite porewater, whose chemistry would be altered over time by the ingress of the Boom Clay constituents with a pH of c. 8.5-9.5.

History of the corrosion studies

An extensive corrosion programme on various candidate overpack materials and construction materials for galleries and boreholes considered in the final disposal of HLW and SF was initiated by the Belgian Nuclear Research Centre (SCK CEN) in the mid-1970s. This programme received the financial support of ONDRAF/NIRAS and the European Commission (EC). The main aim of this long-term programme was to evaluate the corrosion-resistance characteristics of the studied metallic materials in the various environmental conditions that can exist during deep underground disposal in clay. A step-wise approach was adopted, consisting of: (1) laboratory screening studies; (2) detailed studies; and (3) demonstration tests.

Laboratory screening studies

In the first step, laboratory screening studies (1974– *c*. 1983) were performed on a wide range of metallic materials, for example:

- a large number of corrosion-resistant materials, including ferritic stainless steels (AISI 430, 1803 T and 1803 MoT);
- austenitic stainless steels (AISI 304, AISI 304L, AISI 316, AISI 316L and UHB 904L);
- Ni and its alloys (Ni 200, Inconel 600, Inconel 625, Incoloy 800, Hastelloy B and Hastelloy C-4);
- Ti and its alloys (IMI 115, Ti/0.2Pd, Ti6Al4V and Ti5Al2Sn);
- Al and its alloys (technical pure Al, AA-5052H-32 and AA-6061T-8); and
- · Cu and its alloys.

The test materials also included some corrosion-allowance materials, such as carbon steel (ST-37) and chromized carbon steel. These were tested as potential candidate overpack materials. For the construction of the linings of the disposal galleries and boreholes, with a significantly shorter projected lifetime of 50-100 years, different grades of unalloyed and alloyed cast iron (grades 42, 50 and 60) were considered (Casteels et al. 1981; Dresselaers et al. 1982; Accary 1985; Haijtink 1985). An overview of the metals tested during the screening studies is given in Tables 1 and 2.

The screening studies included both accelerated tests and exposure tests in order to classify the corrosion behaviour of the tested metallic materials and to make a first selection of the most promising candidate overpack materials. The alloys were tested in the annealed (as-received) and heat-treated condition. The heat-treatment simulated the temperature-time-dependence profile determined by the process used for pouring the vitrified radioactive waste into the waste canisters, as defined by the French Ateliers de Vitrification Marcoule (AVM). Welded and stressed (U-bend and threepoint loading) specimens were also included in the tests, both in their polished and unpolished conditions.

The experiments were conducted in direct contact with clay, interstitial clay water, humid clay atmosphere and Antwerpian groundwater under both aerated and deaerated conditions at a temperature range of between 2 and 300°C. The experiments lasted for up to 4 years. In general, the corrosion rate was determined from weight-loss measurements. However, some of the test cells were also equipped with an online corrosion-rate system (CORRATER[®]) measurement probe), which was based on linear polarization resistance (LPR) measurements (Casteels et al. 1980, 1981; Shahid 1980; Dresselaers et al. 1982; Accary 1985; Dresselaers and Tas 1985; Haijtink 1985; Tas et al. 1987).

Thick-walled AISI 316 autoclaves, operated at 25, 100, 150 and 300°C, were used to carry out the tests in direct contact with clay. The clay with which the autoclaves were filled came from Boom Clay samples taken at the Mol site. Besides autoclave tests, 'field' experiments were carried out between 1979 and 1983 in a surface clay quarry at Terhaegen, Belgium (Fig. 4). The quarry is situated about 50 km to the west of Mol where the same Boom Clay has been exploited to manufacture building bricks. The metallic samples were mounted on steel tubes buried in sleeves in the geological clay formation at a depth of about 1 m. Three test tubes, operated at 13, 50 and 150°C, were installed in the clay formation at Terhaegen (Casteels et al. 1981; Dresselaers et al. 1982; Dresselaers and Tas 1985; Haijtink 1985; Tas et al. 1987; Debruyn and Tas 1988).

The tests in a humid clay atmosphere were carried out under dynamic conditions either in a corrosion chamber (50°C) or in inert furnaces (at 150 and 300°C). The atmosphere used was a synthetic one simulating the atmosphere expected in the boreholes of a geological clay formation corresponding to pyrolysis of the clay at 300°C. The synthetic moisture was composed of an air stream loaded with water vapour, with a known relative humidity, and corrosive agents, such as SO₂. The composition of the moisture is given in Table 3. The corrosion chambers (50°C) operated with alternating periods of 30 min each for heating and vaporizing the corrosive moisture. The corrosion chamber loaded with

Material		С	hemical co	mposition (wt%)	
	С	Si	Mn	Р	Ni	Cr
Non-alloved grades						
Grade 42	3.7	2.5		0.03		
Grade 50	3.7	2.5	0.4	0.03		
Grade 60	3.7	2.4	0.5	0.03		
Alloyed grades						
Ni-alloyed cast iron (grade D ₂ , c. 19.5% Ni)	2.9	2.0	0.9	0.02	19.5	2.16
Si-alloyed cast iron (c. 6% Si)	2.4	5.8	0.4	0.02	0.85	
Ni-alloyed cast iron (c. 2.5% Ni)	3.8	2.3		0.02	2.42	

Table 1. Selection of cast nodular irons (with their chemical composition in wt%) and the applied coating systems tested during the screening corrosion testing programme as potential structural materials (Dresselaers et al. 1982; Haijtink 1985)

Anti-corrosive coatings applied to cast iron grades 42 and 60

1 Galvanization treatment (150 µm)

2 Galvanization treatment (150 μm) + phosphate coating + coal tar epoxy primer layer (50 μm) + coal tar epoxy 'high-build' layer (150 μm) + coal tar epoxy finish layer (50 μm)

3 Coal tar epoxy primer layer (50 μm) + coal tar epoxy 'high-build' layer (150 μm) + coal tar epoxy finish layer (50 μm)

4 Galvanization treatment (150 μm) + polyurethane primer layer (40 μm) + coal tar epoxy 'high-build' layer (160 μm) + coal tar epoxy finish layer (50 μm)

5 Coal tar epoxy primer (80 μm) + coal tar epoxy 'high-build' layer (160 μm) + coal tar epoxy finish layer (50 μm)

6 Coal tar epoxy primer layer $(40 \ \mu m)$ + epoxy solvent-free layer $(200 \ \mu m)$

7 Galvanization treatment $(150 \,\mu\text{m})$ + polyurethane primer layer $(40 \,\mu\text{m})$ + epoxy solvent-free layer $(200 \,\mu\text{m})$

Organic coatings were applied after hot dipping in Zn at 450°C. Galvanized specimens were treated in a phosphating solution prior to the application of the paint and plastic coatings. Specimens in the as-received condition were shot peened according to SAE standards to a surface finish of SAE 2.5.

various specimens is shown in Figure 5. The tests at 150 and 300°C were performed in inert furnaces in which $14.51 h^{-1}$ of air loaded with 3.5 ml h^{-1} of moisture was injected (Casteels *et al.* 1980, 1981; Shahid 1980; Dresselaers *et al.* 1982; Accary 1985; Dresselaers and Tas 1985; Haijtink 1985; Tas *et al.* 1987).

The static tests in interstitial clay water and Antwerpian groundwater were carried out in 1.51 sealed borosilicate flasks with an air cover at 49 and 98°C. The composition of the interstitial clay water and the Antwerpian groundwater is given in Tables 4 and 5, respectively. The composition of the interstitial clay water was determined by chemical analysis of water that was equilibrated with clay at different temperatures. The Antwerpian groundwater represented the composition of the water present in the sandy formations just above the Boom Clay Formation, which at that time was believed to be the main source of water intrusion in a DGR located at Mol at a depth of 225 m (i.e. in the middle of the Boom Clay Formation). The experimental set-up of the corrosion experiments in interstitial clay water is shown in Figure 6 (Casteels et al. 1981; Dresselaers et al. 1982;

Accary 1985; Dresselaers and Tas 1985; Haijtink 1985; Tas et al. 1987).

Further insights into the long-term corrosion behaviour of cast iron were obtained by post-test examination of cast-iron samples recovered from underground structures (shafts) of the old coal mines of Winterslag and Ressaix (in Belgium). These samples had been exposed to marlstone (a sedimentary rock composed of a mixture of clay and limestone) for periods of up to 90 years (Dresselaers *et al.* 1982; Dresselaers and Tas 1985; Tas *et al.* 1987).

Furthermore, the effect of gamma (γ) radiation on the corrosion rate of a limited set of candidate overpack materials (ST-37 grade carbon steel, AISI 316 and UHB 904L grades stainless steel, Inconel 625 and Hastelloy C-4 grades Ni-alloys, and Ti/0.2Pd grade Ti-alloy) was evaluated. The corrosion tests were carried out in the Research Irradiation for Technological Application (RITA) facility. This facility is installed in the hydraulic loop of the BR2 reactor (Belgian Reactor 2) and consists of four symmetrically positioned ⁶⁰Co sources 7 m below the water surface, creating a fairly homogeneous radiation field of 10³ Gy h⁻¹. The radiation installation is composed of an outer watertight stainless steel container,

Ti (and its alloys) IMI 115

Ti6Al4V

0.2Pd) Al (and its alloys)

Al

Ti5Al2Sn

IMI 260 (Ti/

AA-5052H-32

AA-6061T-8

0.03

0.05

0.15

0.19

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Material					Chemical	compos	ition (wt%	6)			
	Fe	Cr	Ni	Mn	Mo	Si	Ti	A1	C	N	Others
	10	CI	141	IVIII	1010	51	11	7 11	C	11	Others
Carbon steel											
ST-37	bal		0.015	0.25					0.037	0.003	
Chromized steel											
Cockerill	bal	22.90	0.14	0.02		0.34			0.063	0.0060	
Ferritic stainless	steel										
AISI 430	bal	16.50				0.31			0.045	0.0255	
1803 T	bal	17.50		0.56		0.82	0.51		0.017	0.019	
1803 MoT	bal	17.80		0.44		0.35	0.54		0.016	0.016	
Austenitic stainle	ss steel										
AISI 304	bal	18.12	8.34	1.44	0.08	0.42			0.048	0.0465	
AISI 304L	bal	17.80	9.10	1.10	0.16				0.019	0.0196	
AISI 316	bal	17.80	10.8	1.63	2.13	0.56			0.030	0.0315	
AISI 316L	bal	15.1	12.55	0.69	2.90				0.020	0.161	
UHB 904L	bal	18.85	26.34	1.12	4.49	0.44			0.014	0.0497	
Ni (and its alloys)										
Ni 200	, 	0.2	bal	0.32	0.05	0.5	0.02		0.010		
Inconel 600	10.40	10.6	bal	0.50		0.30	0.21		0.034	0.220	
Inconel 625	3.51		bal	0.10	8.85	0.2	< 0.02		0.021		
Incoloy 800	41.50	17.6	bal	0.70		0.30	0.35		0.038	0.0250	
Hastelloy C-4	1.10	6.6	bal	0.34	12.50	0.25			0.002	0.0190	
Hastelloy B	1.80	0.3	bal	0.56	23.20	0.5	0.01		0.014	0.0050	

0.00065

0.015

< 0.01

0.335

Table 2. Selection of candidate overpack materials (with their chemical composition in wt%) tested during the screening corrosion testing programme (Casteels et al. 1981; Accary 1985)

bal, balance (i.e. the fraction of the component to reach 100% composition).

< 0.01

0.13

in which an inner sample basket is inserted. The sample basket is made up of several aluminium plates that are stacked on top of each other. Heating was achieved by means of electrical resistance wires that were fixed between the aluminium plates. Cylindrical holes (37 in total) were drilled in the aluminium plates to house the different test assemblies. The test assemblies consisted of Pyrex[®] flasks that were filled with the corrosive media and in which the metallic samples were placed. Figure 7 illustrates the set-up used to perform the corrosion tests under γ radiation (Haijtink 1985, 1986; Debruyn *et al.* 1987, 1988).

The metallic samples were exposed to either synthetic interstitial clay water or clay water slurries for periods up to 42 days at 90°C under oxidizing or reducing conditions (by using either air or argon as the cover gas above the test media). The synthetic test solutions used in these studies corresponded with interstitial clay water in equilibrium, either with fully oxidized clay or with undisturbed clay as removed from the geological host formation. The compositions of the interstitial clay water in equilibrium with oxidized clay or with clay under reducing conditions are given in Tables 6 and 7, respectively. The clay water slurries were prepared by mixing 100 g of clay in 1 l of distilled water. The metals were tested in three different conditions: as-received, heat-treated and welded (Haijtink 1985, 1986; Debruyn *et al.* 1987, 1988).

V: 3.12

Sn: 2.4

Pd: 0.57

0.0005

Detailed studies

0.053

0.1

0.51

< 0.12

bal

bal

bal

bal

0.01

0.05

< 0.05

6.0

5.2

bal

bal

bal

Based on the outcome of a broad laboratory screening programme, the extensive list of tested metallic materials was significantly reduced to a more limited



Fig. 4. View of the test site (top left) and the experimental set-up (bottom right) of the 'field' experiments carried out in a surface clay quarry at Terhaegen, Belgium (Shahid 1980).

selection of candidate overpack materials for further testing under specifically selected conditions. These studies involved *in situ* experiments and laboratory experiments. An overview of the metals tested during the *in situ* corrosion programme and the laboratory corrosion programme is given in Tables 8 and 9, respectively.

The *in situ* corrosion test tubes (loaded with metallic overpack samples, as well as wasteform samples) were amongst the first tests performed in the HADES URL. These *in situ* tests were designed in the early 1980s, on the basis of the experience gained with similar 'field' experiments carried out

Table 3. Composition of synthetic gas (moisture) (in ppm) used in the screening studies (Casteels et al. 1980, 1981; Shahid 1980; Dresselaers et al. 1982; Accary 1985; Haijtink 1985, 1986)

HCl	H_2SO_4	HF	NaCl	CaF_2	KF	$MgCl_2$	pН
4.9	15	0.40	8	0.21	0.44	0.1	3.5

in a clay quarry at surface level (at Terhaegen in Belgium) (Debruyn and Tas 1988; Van Iseghem *et al.* 1993, 2003).

The *in situ* corrosion experiments basically consisted of placing metallic coupons (and wasteform samples) on the outside or the inside of a steel support tube, heated from the inside, and exposing the coupons for up to 7.5 years either directly to Boom Clay or to a humid clay atmosphere (saturated or not with concrete pore solution) emanating from the clay host rock formation. This set-up allowed study of the corrosion behaviour under conditions that approached 'real' disposal conditions as closely as possible (Kursten *et al.* 2004*c*; Kursten and Druyts 2006). It is important to keep in mind that these experiments were designed based on the SAFIR-1 concept, which was at that time the reference disposal concept.

Owing to the heat generated by the radioactive waste, the temperature in the clay in the immediate vicinity of the overpack will increase. Therefore, corrosion experiments were not only carried out at 16° C, which is the natural clay temperature of the Boom Clay Formation at 225 m depth, but also at two higher temperatures: 90 and 170°C. The highest

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Fig. 5. Experimental set-up used to perform corrosion experiments in a humid clay atmosphere (Shahid 1980).

temperature (170°C) does not correspond to real repository conditions, which is expected to be well below 100°C, but was chosen to accelerate the damage mechanisms operating at lower temperatures and/or trigger corrosion mechanisms with excessive incubation times at lower temperatures (Debruyn *et al.* 1989*b*, *c*, 1991; Kursten *et al.* 1997).

The influence of γ radiation on the corrosion behaviour of the candidate overpack materials was also investigated *in situ*. The CERBERUS (Control Experiment with Radiation of the BElgian

Table 4. Composition of the interstitial clay water $(g \cdot l^{-1})$ used in the screening studies (Shahid 1980; Casteels et al. 1981; Accary 1985)

Compound	Concentration $(g l^{-1})$
$\begin{array}{c} Na_2SO_4 \\ NaCl \\ K_2SO_4 \\ MgSO_4.7H_2O \\ CaSO_4.2H_2O \\ CaCO_2 \end{array}$	16.266 0.158 1.24 16.639 c. 10.071 (saturated) c. 7.5 (saturated)
,	ci (outurated)

Table 5. Composition of Antwerpian groundwater $(mg l^{-1})$ used in the screening studies (Shahid 1980; *Casteels* et al. 1981; Accary 1985)

Compound	Concentration $(mg l^{-1})$
$\begin{array}{c} SiO_2 \\ Na \\ K \\ Mg \\ Ca \\ Pb \\ F^- \\ PO_4^{3-} \\ Free CO_2 \\ CO_3^{2-} \\ Organic species \\ Cl^- \\ SO_4^{2-} \\ NO_3^- \\ Fe \\ Cu \\ Sn \\ pH \end{array}$	$\begin{array}{c} 8.05 \\ 63.4 \\ 7.4 \\ 3.57 \\ 21.3 \\ \leq 1 \times 10^{-3} \\ 0.817 \\ 53 \times 10^{-3} \\ 6 \\ 188 \\ 3.7 \\ 35.5 \\ > 0.5 \times 10^{-3} \\ 5.95 \times 10^{-3} \\ 0.189 \\ \leq 10 \times 10^{-3} \\ \leq 10 \times 10^{-3} \\ 7.35 \end{array}$

Repository for Underground Storage) *in situ* experiment was developed to simulate the near-field effects in an argillaceous environment of a Cogéma HLW canister after 50 years of cooling time. The radiation and thermal field expected around such a canister was generated by a ⁶⁰Co source (dose rate of 400 Gy h^{-1}) and a heating system. A total of seven different types of metallic materials were studied:

- (1) EEG Usinor grade carbon steel;
- (2) AISI 309 grade stainless steel;



Fig. 6. Experimental set-up used to conduct the corrosion experiments in interstitial clay water and Antwerpian groundwater (Casteels *et al.* 1985; Haijtink 1985).



Fig. 7. Experimental set-up used to perform the corrosion tests under γ radiation: (a) outer watertight stainless steel container, (b) inside view of the stainless steel container (with sample basket) and (c) inner aluminium sample basket (with mounting of some Pyrex[®] flasks) (Haijtink 1986).

- (3) AISI 316Ti grade stainless steel;
- (4) Hastelloy C-4 grade nickel alloy;
- (5) IMI 115 grade titanium alloy;
- (6) Ti/0.2Pd grades titanium alloy; and
- (7) Copper.

The samples were exposed to Boom Clay for a period of about 8.5 years, of which about 5 years was in a radiation field at 80–85°C. Figure 8 shows a schematic view of the CERBERUS *in situ* experiment (Kursten and Van Iseghem 1998*a*; Van Iseghem *et al.* 2003).

The laboratory corrosion programme was primarily aimed at: (1) performing accelerated tests to obtain information on long-term processes; and (2) investigating the influence of several parameters on the susceptibility to localized corrosion (with a

Table 6. Composition of the interstitial clay water $(g l^{-1})$ in equilibrium with oxidized clay used in the γ -radiation experiments (Haijtink 1985, 1986; Debruyn et al. 1987, 1988)

Compound	Concentration (g l ⁻¹)
$\begin{array}{c} Na_2SO_4\\ K_2SO_4\\ MgSO_4\\ CaSO_4 \end{array}$	13.92 0.87 19.19 3.61

Table 7. Composition of the interstitial clay water $(mg \ l^{-1})$ in equilibrium with clay under reducing conditions used in the γ -radiation experiments (Debruyn et al. 1987, 1988)

Compound	Concentration (mg l^{-1})
Na ₂ SO ₄	39.8
MgSO ₄	15.0
NaF	10.1
Na ₂ CO ₃	74.2
NaHCO ₃	13.4
KCl	39.4
NaCl	19.9

distinct emphasis on pitting corrosion). Considering the type of the studied candidate overpack materials and the nature of the underground disposal environment, it was believed at that time that pitting corrosion posed the main threat to the integrity of the overpack. This form of localized attack can cause significant wall thickness penetration in a relatively short period of time and, hence, lead to a significant release of radionuclides. The various parameters that were investigated were:

- temperature (up to 140°C);
- type of backfill (Boom Clay or bentonite);
- presence of aggressive species (Cl⁻, SO₄²⁻ or $S_2O_3^{2-}$);
- oxygen content (oxic v. anoxic conditions);
- presence of a γ -radiation field (dose rate of 1000 Gy h⁻¹); and
- influence of radiolysis products (Kursten *et al.* 2001, 2004*c*; Kursten and Druyts 2006).

The laboratory experiments included electrochemical experiments, immersion tests and specific experiments investigating the susceptibility to stress corrosion cracking (SCC). The electrochemical experiments involved determining critical pit nucleation potentials (E_{NP}) and repassivation potentials (E_{PP}) by cyclic potentiodynamic polarization (CPP) measurements and by monitoring the corrosion potential (E_{CORR}) as a function of time in media representative of the DGR conditions. The pitting susceptibility was assessed by comparing the value of E_{CORR} to the values of E_{NP} and E_{PP} . The immersion tests can be regarded as complementary to the in situ corrosion experiments in the sense that the immersion tests are much more flexible for studying the medium-term interactions between candidate overpack and backfill materials under a wide range of different conditions (Kursten et al. 2001, 2003, 2004c).

Demonstration tests

In addition to the laboratory parametric corrosion experiments, demonstration tests were also

Material							Chemi	cal compositio	n (wt%)		
Identification	Description	Fe	Cr	Ni	Mn	Мо	Si	Ti	С	Ν	Others
Canister materi AISI 309* AISI 430 [†] AISI 316Ti [‡]	als Austenitic SS Ferritic SS Austenitic SS	bal bal bal	23 16.50 16–18	13 10–14	2.0 <2.0	2–3	1.0 0.37 <1.0	>5 × %C	0.20 0.045 <0.08	0.026	
Candidate over EEG Usinor	pack materials Low carbon steel	bal	0.02	0.04	0.67	< 0.01	0.27	< 0.01	0.11		P: 0.02; S < 0.01; Al: 0.04; Cu: 0.015: Sn < 0.01
1803 MoT AISI 316 UHB 904L Inconel 625	Ferritic SS Austenitic SS Austenitic SS Ni alloy	bal bal bal 3.57	18.07 17.80 18.65 12.20	0.28 10.80 26.34 bal	0.28 1.63 1.12 0.10	2.07 2.13 4.49 8.85	0.27 0.56 0.44 0.20	0.36 <0.02	0.030 0.014 0.021	$\begin{array}{c} 0.009 \\ 0.032 \\ 0.050 \\ 0.023 \end{array}$	Cu: 0.12 Nb: 2.7; Ca: 0.005; Mg: 0.02; Al:
Hastelloy C-4 IMI 115	Ni alloy Commercially pure Ti	0.50	15.6	bal	0.22	15.4	0.03	0.11 bal			Co < 0.1
Ti/0.2Pd	Ti alloy	0.06						bal	0.01		Pd: 0.16; V < 0.03; Al: 0.008; Sn: 0.07

Table 8. Selection of metallic materials (with their chemical composition in wt%) tested during the in situ corrosion programme (Haijtink 1986; Kursten et al. 1997, 2004a, b, c; Kursten and Van Iseghem 1999)

SS, stainless steel; bal, balance (i.e. the fraction of the component to reach 100% composition).

*Grade of ferritic stainless steel used to fabricate the drums to store the bituminized intermediate-level radioactive waste produced at the Eurochemic/Belgoprocess pilot reprocessing plant (Mol-Dessel, Belgium).

⁴Grade of austenitic stainless steel (Ti stabilized) used to fabricate the drums to store the vitrified high-level radioactive waste coming from the Pamela reprocessing plant.

1999; Kursten et al.	2004a, b, c)			ſ				1					•
Material							0	Chemical	composit	ion (wt%	(
Identification	Description	F	Cr	ïZ	Mn	Мо	Si	Τï	С	S	Р	z	Others
Candidate overpac	k materials												
TStE 355	Carbon steel	bal	0.03	0.03	1.12		0.34	0.003	0.18	0.002	0.01	0.005	Nb: 0.017
AISI 309S	Austenitic SS	bal	22.58	13.51	1.7		0.33		0.063	0.002	0.021		
AISI 316L	Austenitic SS	bal	16.9	11.0	1.54	2.08	0.54		0.017	0.001	0.032		
AISI 316L hMo	Austenitic SS	bal	17.67	12.53	1.16	2.84	0.61		0.015	0.001	0.030		
AISI 316Ti	Austenitic SS	bal	16.8	10.7	1.08	2.05	0.40	0.3	0.044	0.009	0.028		
UHB 904L	Austenitic SS	bal	19.7	25.0	1.48	4.47	0.19		0.019	0.001	0.019	0.08	Cu: 1.51
Cronifer 1925hMo	High-alloyed SS	bal	20.6	24.85	0.92	6.4	0.30		0.005	0.002	0.018	0.198	Cu: 0.86
Hastelloy C-4	Ni alloy	0.98	15.75	bal	0.04	15.85	0.02	< 0.01	0.003	0.003	0.004		Co: 0.01
Ti/0.2Pd	Ti alloy	0.04						bal	0.01			< 0.01	Pd: 0.16; O ₂ : 0.13; H ₂ : 0.001

Table 9. Selection of metallic materials (with their chemical composition in w1%) tested during the laboratory parametric corrosion programme (Druyts and Kursten

developed with the aim of demonstrating (on a large scale) the feasibility of constructing a DGR and/or to confirm the corrosion rates and phenomena measured and observed in the previous *in situ* and laboratory experiments. The main focus of these tests was to study integrated effects and processes, such as the interactions between the waste, overpack and clay, combined with sorption and migration effects in the clay (Van Iseghem *et al.* 2003; Kursten and Druyts 2006).

A first demonstration experiment, called the OPHELIE mock-up (On-surface Preliminary Heating simulation Experimenting Later Instruments and Equipment), was constructed on the surface in 1997. The primary aim of this large scale mock-up experiment was to review several technical aspects of the disposal concept, such as the installation of the backfill material, the stainless steel disposal tube and the monitoring devices. The mock-up consisted of a 5 m-long steel cylinder with a diameter of 2 m. This simulated a section of a disposal gallery as envisaged in the SAFIR-2 concept. The concrete gallery lining was replaced by a stainless steel liner, which was designed to resist the internal pressure caused by the swelling pressures of the backfill material (due to hydration). A stainless steel tube with a diameter of 0.5 m was installed in the centre of the cylinder, representing the disposal tube. This central tube contained heating elements that dissipated heat at a power of 450 W m^{-1} , which is comparable to the heat dissipated by the vitrified HLW waste packages. The annular gap between the central tube and the outer liner was backfilled with pre-compacted blocks of a clay-based material (i.e. a mixture of FoCa clay, sand and graphite) that were placed in three concentric rings around the central steel tube (Dereeper and Verstricht 2002; Verstricht and Dereeper 2003). Figure 9 shows a general view of the mock-up during assembly, along with a comparison with the crosssection of a disposal gallery. Although the OPHELIE mock-up experiment was initially designed as a large-scale hydration test under the thermal load of pre-fabricated bentonite blocks, and not as a corrosion experiment as such, the analysis of the stainless steel central tube and liner has led to an increased understanding of the corrosion processes that the could metallic overpack face under real disposal conditions.

Another demonstration test, named CORALUS (CORrosion of Active gLass in Underground Storage conditions), was one of the latest generations of *in situ* experiments that was installed in the HADES URL. This experiment integrated many different parameters and processes that are expected in a DGR (Valcke *et al.* 2001, 2006; Jockwer and Wieczorek 2006). Examples of parameters that were considered in CORALUS are α and γ irradiation, temperature, realistic geochemical conditions,

stainless steel; bal, balance (i.e. the fraction of the component to reach 100% composition)

SS,



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Fig. 8. Design of the CERBERUS in situ experiment (Van Iseghem et al. 2003).

pressure, and backfill material. Examples of processes are the interactions with the host formation at *in situ* pressure, dissolution, radiolysis, migration and sorption, and the coupling between these. The CORALUS experiment consisted of four modular test tubes containing inactive and α -active glass



Fig. 9. The on-surface OPHELIE mock-up experiment: (**a**) general view of the cross-section of the mock-up during assembly (showing the backfill blocks, the hydration tubes, the disposal tube and the sensor cabling) and (**b**) schematic view of the cross-section of a HLW disposal gallery (according to the SAFIR-2 reference design) (Kursten and Druyts 2005).

samples in direct contact with a backfill material. Each test tube was divided into three independent modules. Each module consisted of an inner support tube with flanges and an outer support tube with permeable filter elements. The residual space between the inner and outer support tubes was filled with a different type of backfill material (pre-compacted semi-cylindrical blocks):

- dried Boom Clay;
- mixture of 60 wt% FoCa clay, 35 wt% sand and 5 wt% graphite; and
- mixture of 95 wt% FoCa clay and 5 wt% inactive glass powder.

The glass and the metallic samples were mounted in square openings machined either in the inner support tube or in a flange. Piezometers were installed to enable the online measurement of the *in situ* pH and redox potential. The test tubes also included heating elements, thermocouples and (for two test tubes) ⁶⁰Co sources. The γ -irradiation doses to which the samples were subjected were roughly the same as during the CERBERUS *in situ* test (simulating the γ -irradiation field of a real HLW canister). The test tubes were operated at two different temperatures (30 and 90°C) for durations of between 1.3 and 10 years (Neerdael and Volckaert 2001; Valcke *et al.* 2001, 2006, 2007; Jockwer and Wieczorek

2006; Aertsens and Valcke 2009). Figure 10 shows a 3D cut-away view of a test tube, together with a picture of a part of a module during its assembly.

During the operational phase of the CORALUS *in situ* experiment, the disposal design changed. The SAFIR-2 concept (stainless steel overpack surrounded by clay) was replaced by the supercontainer concept (carbon steel overpack embedded in concrete). As a result, the outcome of the test results became less relevant and therefore the corroded metallic samples were not analysed.

Rationale behind the corrosion studies

In the first phase, screening studies were performed on a large number of metallic materials in order to make a classification of their corrosion behaviour, thereby enabling a first selection of the most promising candidate overpack materials to be made. Numerous testing methods were used in these studies: accelerated experiments involved testing in a laboratory, such as static tests in borosilicate flasks (interaction with interstitial clay water and Antwerpian groundwater) and dynamic tests in corrosion chambers and inert furnaces (interaction with a humid clay atmosphere). Exposure tests (direct contact with clay) were conducted either in a 'surface laboratory' (in steel autoclaves) or in a 'surface



Fig. 10. The CORALUS *in situ* experiment: (a) three-dimensional cutaway of a test tube with 60° C sources and (b) general view of one module showing the inner support tube, bottom flange and connection flange of the module (Valcke *et al.* 2006).

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clay quarry' at Terhaegen ('field' experiments). Also, specific test set-ups were included to study susceptibility to SCC (U-bend specimens and threepoint loading) and the effect of γ irradiation (RITA radiation facility installed in the BR2 reactor).

In the second phase, more detailed studies were performed on a limited selection of candidate overpack materials, involving in situ and laboratory experiments. The *in situ* experiments allowed study of the corrosion behaviour (e.g. corrosion rate) of metallic coupons under conditions as close as possible to 'real' disposal conditions. The reasoning at that time was that the lifetime of the overpack could be predicted by extrapolating the uniform thickness reduction, which was calculated from the medium-term in situ tests (maximum duration of 7.5 years) to periods of up to a few thousand years (at that time, the corrosion-allowance material carbon steel was considered as a primary candidate overpack material) (Kursten et al. 1997, 2001, 2004c; Kursten and Druyts 2006).

On the other hand, a second important category of in situ experiments involved the characterization of the clay host-rock environment in terms of pH and Eh, and the chemical composition of the interstitial clay water. These measurements aimed to identify the evolution of the repository chemistry in the immediate vicinity of the metallic overpacks. This information was essential in conceiving additional laboratory experiments for corrosion-rate evaluation under conditions deviating from the undisturbed formation conditions (i.e. more stringent conditions and accident scenarios). It was believed that this would allow definition of safety margins accounting for certain corrosion-rate abnormalities and thus determination of the extra wall thickness needed to ensure the long-term integrity of the metallic overpack (Debruyn and Tas 1988; Van Iseghem et al. 2003).

Simultaneously, immersion and laboratory experiments (complementary to the *in situ* corrosion experiments) were conducted to investigate the influence of several parameters such as, for example, temperature, type of backfill (Boom Clay or bentonite), presence of aggressive species (Cl⁻, SO₄²⁻ or S₂O₃²⁻), oxygen content (oxic v. anoxic conditions) on pitting corrosion. *In situ* experiments (e.g. CER-BERUS) were launched to evaluate the effect of γ irradiation and radiolysis products on the corrosion rate (Kursten *et al.* 2001, 2004*c*; Kursten and Druyts 2006).

Gradually, the emphasis shifted from basic research to large-scale integrated demonstration experiments in which a number of interacting components and/or processes were simultaneously studied. Although these experiments were initially not designed as corrosion experiments – their main goal was demonstrating the technical feasibility and overall safety of a DGR in the Boom Clay Formation – they provided an opportunity to include several candidate metallic overpack materials. The advantage of these set-ups was that they integrated many different parameters and processes (and their coupling), thereby enabling study of the performance of the metallic samples in direct contact with clay under conditions as representative as possible of those expected to prevail in a DGR in the Boom Clay Formation.

The role of the HADES URL in corrosion research

The HADES URL has played an important role in gaining a better understanding of various processes that might affect the long-term safety of disposal in clay, such as the corrosion of the metallic overpack, because it allowed study of the corrosion behaviour of candidate overpack materials under conditions that approached 'real' disposal conditions as closely as possible. Such conditions are very difficult (if not impossible) to simulate in the laboratory. The main advantage of in situ testing is that it enables maximization of the degree of integration and reality: interaction with the host formation at in situ pressure, in realistic geochemical conditions, natural shielding against γ irradiation, etc. (Kursten *et al.* 2004c; Kursten and Druyts 2006; Valcke et al. 2006, 2007).

The corrosion experiments were among the first experiments to be installed in situ in the HADES URL in the mid-1980s. The in situ tests that were designed and operated later (e.g. BACCHUS, CAC-TUS, MEGAS, PHEBUS, RESEAL, CERBERUS, CORALUS and PRACLAY) have benefitted greatly from the expertise that was gained from these 'firstgeneration' in situ tests. During the corrosion experiments, a lot of pioneering research was done in different areas of *in situ* testing, for example: design, installation, operation and retrieval of in situ experiments (e.g. an in-house overcoring technique to retrieve the test tubes was developed), measurement of pH and Eh of interstitial clay water, sampling of interstitial clay water (installation of piezometers), and instrumentation for online monitoring of the clay environment (e.g. temperature, pressure and hydration).

Several publications have presented the various advantages that testing in a URL offers compared to laboratory testing (Heinonen and Raynal 2001; OECD/NEA 2001):

 A URL provides an excellent opportunity to conduct *in situ* investigations to increase basic understanding of the geological, hydrogeological, geochemical, structural and mechanical properties of the host rock, to study its response to imposed changes, and to acquire data required for safety assessments.

- In a URL, equipment and methods for *in situ* characterization of different host rocks can be tested and improved.
- The host rock as a geological barrier and its disturbance induced by repository excavation, thermal loading, gas generation and chemical interactions can all be characterized in a URL.
- The feasibility of the repository design and of the behaviour and performance of various components of the repository can be tested in a URL (e.g. repository construction, waste emplacement and retrieval, construction of engineered barriers, repository sealing, and closure).
- The construction of a URL offers an excellent opportunity to test and optimize different excavation methods and lining systems.

The importance of conducting corrosion experiments under realistic disposal conditions, and the role URLs can play in this regard, was already recognized in the late 1980s. In an International Atomic Energy Agency (IAEA) Technical Committee Meeting, held in 1986 (Popp *et al.* 1987), it was recommended that tests in realistic environments corresponding with normal and accidental conditions should be carried out to qualify and apply corrosion-monitoring techniques for corrosion evaluation under real DGR conditions and to develop corrosion and near-field evolution models (Kursten *et al.* 1997).

Several international reviews have commented on the usefulness of *in situ* testing and the importance of underground research facilities (such as the HADES URL) in the *in situ* testing strategy:

- An international workshop devoted to *in situ* tests on wasteforms and container materials in various candidate rocks, organized in 1992, concluded that *in situ* testing is worthwhile and contributes to characterizing the performance of the waste package constituents (McMenamin 1993).
- Two review papers on underground laboratories emphasized that in addition to the technical interests of underground testing, underground testing is also important for building confidence in proposed disposal concepts and for communicating to the public (McCombie and Kickmaier 2000), and that the output of the *in situ* tests can vary depending on their scale (Brewitz *et al.* 2000).
- The importance of URLs, both for the scientific and technological development of a DGR programme and for building public confidence in radioactive waste deep disposal, was demonstrated by the specific session devoted to URLs that was set up in the framework of the First International Conference on Geologic Repositories (ICGR 1999) held from 31 October to 3

November 1999 in Denver, Colorado, organized by the US Department of Energy and cosponsored by the IAEA (Wu *et al.* 2001).

The Radioactive Waste Management Committee (RWMC) of the Nuclear Energy Agency (NEA) has published several review reports describing the role of URLs in radioactive waste disposal programmes and their value for building confidence in national programmes (OECD/NEA 2001, 2013). The technical experts of the scientific committee concluded that the role of a URL is essential: (i) to perform experiments for developing datasets for model testing, and for developing and demonstrating technologies for repository construction, waste emplacement, and backfilling and sealing under realistic conditions; and (ii) to offer an excellent opportunity to integrate multiple disciplines (e.g. geology, hydrology, microbiology and engineering), build technical teams and gain practical experience that will be invaluable in the future development of a DGR. They mentioned that certain types of information and experience necessary for characterization, construction, operation and closure of a DGR can only be obtained through access to the underground environment. Similarly, confidence in the facility design, host-rock suitability and engineering feasibility can only be gained through underground verification. All of these factors are of importance in building the safety case for a DGR. Finally, they emphasized the value of a URL in enhancing public confidence that a DGR programme has a valid basis and is being pursued in a responsible manner by a trustworthy implementer. The members were convinced that large-scale, long-term, integrated studies can play a key role in raising technical and public confidence.

Experimental set-up of the *in situ* corrosion experiments

Description of the in situ corrosion experiments

Three test concepts were designed to simulate the different environments that are likely to develop in the course of the DGR evolution. The samples were placed either in 'direct contact with clay' (Type I), in contact with a 'humid clay atmosphere' (Type II) or in contact with a 'concrete-saturated clay atmosphere' (Type III).

The Type I and Type II corrosion test tubes were designed and developed in the early 1980s to simulate the conditions likely to occur in the DGR according to the disposal concept prevailing at that time. The first test concept (Type I corrosion tubes) simulated normal long-term DGR conditions exposing

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the metallic samples directly to the clay rock. The latter two concepts simulated accidental conditions during disposal, where gas might eventually penetrate through capillaries within the other engineered barriers before contacting the waste package. The tests involving a clay atmosphere (Type II) also simulated the temporary storage of containers in an underground disposal gallery in which ventilation and a non-uniform heat distribution would give rise to local condensation and vaporization of clay water.

The concept for the Type III corrosion test tubes was designed much later (at the end of the 1980s) to simulate the large amounts of cement that were foreseen to be used in the more recent geological disposal concept, either as gallery lining or as candidate backfill (Van Iseghem *et al.* 1993; Kursten *et al.* 1997; Kursten and Van Iseghem 1998*b*, 1999).

The Type I corrosion test tubes were inserted horizontally into the clay formation. They were connected to the cast-iron linings of the experimental gallery via 76 cm flanges. The tubes were heated by a retractable furnace situated in the tube interior. The furnace consisted of heating wires wound spirally around a stainless steel support tube. The metallic samples were fixed at the outside of the tubes. A schematic drawing of the Type I test tubes together with a photograph taken during installation in the





Fig. 11. Images of an *in situ* Type I corrosion test tube (direct contact with clay): (a) schematic drawing of the tube and (b) general view of the tube during installation in the HADES URL (Kursten *et al.* 2004c).

HADES URL are presented in Figure 11 (Debruyn et al. 1986; Haijtink 1986; Debruyn and Tas 1988; Van Iseghem et al. 1993; Kursten et al. 1997; Kursten and Van Iseghem 1998b, 1999).

The Type II corrosion test tubes were introduced vertically downwards into the clay formation. The section of the tubes loaded with samples was entirely surrounded by a porous filter. The tubes ended in a porous stainless steel plug (pore size of 5 µm). A carrier gas (helium) was used to collect the corrosive products perspiring from the clay through the filter into the tube and recirculated them subsequently over the test samples (He had to be used rather than the more common Ar because of the safety regulations that applied in the URL). The metallic samples were mounted on a Teflon[®] holder, which was heated at the specified temperature using resistance heating. This Teflon® holder could be retrieved and exchanged during the experiment. A schematic drawing of the Type II test tubes along with a photograph of a Teflon[®] sample holder are presented in Figure 12 (Debruyn et al. 1986; Tas et al. 1987; Debruyn and Tas 1988; Van Iseghem et al. 1993; Kursten et al. 1997; Kursten and Van Iseghem 1998b, 1999).

The Type III corrosion test tubes were inserted in an oblique position in the clay formation to facilitate the recovery of the liquids collected during the test operation. These tubes consisted of two experimental parts:

- the end section of the tube allows samples to be placed in direct contact with the clay, similar to the Type I corrosion test tubes; and
- the second section of the tube, exposing the samples to a clay atmosphere equilibrated with concrete, was similar to the Type II corrosion test tubes. The outside of this section consisted of a porous concrete tube, supported by a stainless steel tube, enabling the clay extracts to percolate and contact the samples present in the inner part. The difference with the Type II corrosion test tubes was that no carrier gas was used in the Type III corrosion test tubes.

The carrier gas in the Type II corrosion experiments was used to simulate certain environmental conditions: He represented an anaerobic situation and O_2 represented an aerobic situation. In the Type III experiments, no carrier gas was used. The atmospheric conditions inside the Type III corrosion experiments therefore changed from oxic (representative of the initial aerobic phase of the geological disposal period) to anoxic in the course of the experiment. A schematic drawing of the Type III test tubes, along with photographs of the entire tube and the Teflon[®] sample holder, are presented in Figure 13 (Van Iseghem *et al.* 1993; Kursten *et al.* 1997; Kursten and Van Iseghem 1998*b*, 1999).

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Fig. 12. Images of the second generation *in situ* Type II corrosion test tube (interaction with a humid clay atmosphere: (**a**) schematic drawing of the tube and (**b**) general view of the Teflon[®] holder on which the samples (metallic and wasteform samples) were mounted (Kursten *et al.* 1996).



(1) gallery lining of the URL

(5) outer stainless steel tube

(2) samples exposed to the concrete-saturated clay atmosphere

(3) samples directly exposed to clay (4) porous concrete

(6) heating elements



Fig. 13. Images of an *in situ* Type III corrosion test tube (interaction with a concrete-saturated clay atmosphere: (**a**) schematic drawing of the tube, (**b**) general view of the entire tube and (**c**) general view of the Teflon[®] holder on which the samples (metallic and wasteform samples) were mounted (Kursten *et al.* 1996).

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These corrosion experiments were performed at 16, 90 and 170°C: 16°C is the temperature of the Boom Clay host-rock formation at 225 m depth. Owing to the heat released by the radioactive waste, the temperature in the clay in the immediate vicinity of the container will rise to well above 100°C. A temperature of 170°C was chosen as a maximum temperature within the EC programme (170°C does not correspond with real repository conditions but was chosen from a safety point of view). A temperature of 90°C was arbitrarily chosen as an intermediate temperature (Debruyn *et al.* 1991; Kursten *et al.* 1997; Kursten and Van Iseghem 1998*b*, 1999).

A total of 12 *in situ* corrosion experiments were installed in the HADES URL between 1985 and 1994: four Type I, six Type II and two Type III corrosion experiments. The identification data for the 12 *in situ* corrosion experiments are listed in Table 10.

Materials selection

The corrosion behaviour of 11 different metallic materials was investigated (Table 8): eight were candidate overpack materials and three were stainless steels used to manufacture the HLW canisters (AISI 430, AISI 309 and AISI 316Ti). Three of the candidate overpack materials (low carbon steel, Hastelloy C-4 grade Ni-alloy and Ti/0.2Pd grade Ti-alloy) were reference materials agreed within the Commission of the European Communities (CEC) because they were studied in various geological environments in other European countries (Cornélis and Van Iseghem 1993; Kursten *et al.* 1997; Kursten and Van Iseghem 1999).

The tested metallic samples had two different geometries, depending on the type of corrosion experiment. The samples placed on the Type I corrosion test tubes were welded rings about 100 mm in

Table 10. Identification data for the 12 in situ corrosion experiments installed in the HADES URL in Mol (Cornélis and Van Iseghem 1993; Van Iseghem et al. 1993; Kursten et al. 1997; Kursten and Van Iseghem 1998b, 1999)

Experiment No.	Target temperature (°C)	Test condition	Installation date (day/ month/ year)	Date of reaching target temperature (day/month/ year)	Date of interrupting heating (day/ month/ year)	Retrieval date (day/ month/ year)	Time of exposure (days/days)*
Type I corro	sion experim	ents (horiz	ontal, direct c	contact with cla	ıv)		
1 2 3 4	170 90 90 16	Clay Clay Clay Clay Clay	16.12.1985 21.10.1985 06.02.1986 02.10.1985	16.10.1986 29.08.1986 25.08.1986 02.10.1985	30.07.1991 02.06.1988 13.08.1993	12.09.1991 05.08.1988 16.11.1993 28.11.1990	2096/1748 1019/643 2840/2545 1883/1883
Type II corr	osion experin	nents (verti	ical, humid cla	av atmosphere))		
5 6 7 8 5b 8b	170 90 90 16 90 16	He Air He Air He He	11.1988 17.11.1988 18.11.1988 11.1988 01.09.1993 06.05.1994	23.01.1989 19.11.1988 19.11.1988 11.1988 09.07.1994 06.05.1994	23.07.1989 17.05.1990 21.04.1990 29.07.1996	10.1989 21.05.1990 26.04.1990 14.09.1992 08.08.1996 10.10.1996	$\begin{array}{r}\pm 334/174\\550/544\\524/518\\1399/1399\\1072/751\\888/888\end{array}$
Type III cor	rosion experi	ments (obl	ique, concrete	-saturated clay	atmosphere)	÷.	
9 10	90 16	Air He	03.03.1989 17.02.1993 [§]	30.08.1989 17.02.1993	10.01.1994	06.05.1994 ⁺ 19.02.1996 [∥]	$\frac{1890}{\pm} \frac{\pm}{765^{\ddagger}}$ $\frac{1125}{920^{\$}}$

*Total time of exposure (days)/effective time at target temperature (days).

[†]06.05.1994: retrieval date of the metallic samples situated on the inside of the tube (concrete-saturated clay atmosphere). 21.11.1994: retrieval date of the metallic samples situated on the outside of the tube (direct contact with clay).

⁴Owing to several technical difficulties that occurred during the exploitation of test tube No. 9, the total time of exposure/effective time at target temperature (90°C) was only about 800 days; the temperature was in excess of 60°C for a total period of about 1020 days.

[§]17.02.1993: installation date of the metallic samples on the outside of the tube (direct contact with clay). 13.08.1993: installation date of the metallic samples on the inside of the tube (concrete-saturated clay atmosphere).

¹19.02.1996: retrieval date of the metallic samples situated on the inside of the tube. 18.03.1996: retrieval date of the metallic samples situated on the outside of the tube.

 $^{\$}$ 1125 days: total time of exposure/effective time at the target temperature (16°C) of the metallic samples situated on the outside of the tube (direct contact with clay). 920 days: total time of exposure/effective time at target temperature (16°C) of the metallic samples situated on the inside of the tube (concrete-saturated clay atmosphere).

diameter, 30 mm wide and 2–4 mm thick. Strips of 30 mm were cut from plate material and shaped into rings by cold rolling. The ring-shaped samples were manually slipped onto the outer stainless steel support tubes. They were electrically insulated from each other and from the steel support tube by means of Teflon[®] spacers and a Teflon[®] lining, respectively. The samples mounted on the Teflon[®] sample holders that were suspended inside the Type II and Type III corrosion test tubes were square plates measuring 30×30 mm. The metallic samples were tested in five different initial conditions (Corné-lis and Van Iseghem 1993; Kursten *et al.* 1997; Kursten and Van Iseghem 1999):

- (1) as-received (the most realistic case);
- (2) polished (a condition not representative of any real situation but one that allowed easier comparisons with results of future *in situ* or laboratory experiments and the literature);
- (3) heat-treated (in an argon atmosphere, to simulate the thermal effect generated during the casting of the vitrified radioactive waste);
- (4) edge-to-edge welded (to examine the effect of the tungsten inert gas (TIG) welding technique); and
- (5) welded in a configuration that was likely to reveal susceptibility towards crevice corrosion.

Prior to their installation, all samples were ultrasonically degreased in acetone in an ultrasonic bath, rinsed under running tap water, dried with compressed air, and accurately measured and weighed.

Installation of the in situ corrosion experiments

Each in situ corrosion experiment consisted of a stainless steel carrier tube onto which the metallic samples were mounted. This carrier tube needed to be sufficiently long (c. 5.3 m) to ensure that the samples were placed in clay that was not disturbed by the construction of the URL (a clay layer of about 3 m around the URL was frozen). The installation procedure for the Type I corrosion test tubes is illustrated in Figure 14. In a first step, a borehole was drilled in the clay formation and a flange was connected to the gallery lining. In a second step, the stainless steel carrier tube, which contained the overpack and the wasteform samples, was inserted into the borehole. A stainless steel extension tube was then welded to the stainless steel carrier tube to connect it to the gallery lining. Subsequently, the stainless steel extension tube was, in turn, welded to a smaller flange for fixation to the gallery lining. Then, a retractable furnace was inserted in the interior of the stainless steel carrier tube. Then, finally, the electrical connections (e.g. heating elements and measuring devices) were made (Kursten and Van Iseghem 1999). A

similar procedure was also used for the installation of the Type II and Type III corrosion test tubes.

Attempts to electrochemically characterize (pH and redox potential) the underground Boom Clay environment surrounding the exposed metallic samples were made to obtain valuable information concerning:

- the capacity of the clay formation to recover from the disturbances caused by a drilling operation and exposure to air;
- the long-term chemical stability of the clay after the initial recovery period; and
- possible changes in the overall clay chemistry in the presence of a heat source.

The redox potential (Eh) can be considered representative of the global aggressivity of the clay medium and it integrates the equilibrium potential of the redox reactions active in that medium. The pH and Eh were monitored as a function of temperature and time in the vicinity of the Type I test tubes at the clay–metal sample interface (Haijtink 1985, 1986; Debruyn *et al.* 1986, 1989*b*, *c*, 1991).

In order to measure the Eh in situ, the Type I test tubes were equipped with Pt and Au electrodes. The potential difference between the inert Pt or Au electrodes was measured against an external reference electrode. As the reference electrode, a solid-body type Ag-AgCl electrode was introduced into the clay formation through an opening in the gallery lining closest to the test tube. The Ag-AgCl reference electrode was filled with a KCl-containing acrylic resin. This resin did not require regular renewal and was pressure resistant. It therefore also did not require complicated additional external pressure compensation. The body of the reference electrode was inserted into a metallic housing to protect it against localized high pressures (Tas et al. 1987; Debruyn and Tas 1988; Debruyn et al. 1991).

The pH in the immediate vicinity of the Type I test tubes was monitored using commercial high-pressure-resistant glass electrodes, which were modified to resist local high pressures. The same Ag–AgCl type electrode as the one used in the Eh measurements was used (Debruyn *et al.* 1986, 1991; Tas *et al.* 1987; Debruyn and Tas 1988).

In addition, measurements of the corrosion potential (E_{CORR}) of as-received and polished carbon steel samples were carried out. E_{CORR} provides instantaneous information concerning the thermodynamic equilibrium between the metal surface and its environment. The potential difference between the corroding carbon steel samples and a reference electrode (the same Ag–AgCl type electrode as the one used for measuring the Eh) was measured. Four carbon steel samples (two as-received and two polished) were mounted on the outer side of an electrically insulated metallic housing in which an Ag–AgCl

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Drilling a borehole and connecting the flange to the gallery lining of the URL.



Welding an extension tube to the stainless steel carrier tube for connection to the gallery lining.



Introducing the stainless steel carrier tube loaded with the overpack and wasteform samples in the borehole.



Welding the steel extension tube to a smaller flange for fixation to the gallery lining.



Inserting a retractable furnace in the interior of the stainless steel carrier tube.



Making the electrical connections (heating elements, measuring devices).

Fig. 14. Installation procedure of the Type I corrosion experiments in the HADES URL (Kursten and Van Iseghem 1998b).

reference electrode was inserted. The probe was implanted *in situ* in a freshly drilled 5 m-long borehole to ensure that the electrodes were exposed to undisturbed clay. A small-diameter borehole (c. 7 cm) was chosen in order to accelerate the contact between the electrodes and the solid clay (Debruyn *et al.* 1990*b*, 1991).

In addition, several probes were introduced into the clay formation for direct corrosion-rate

monitoring. Two types of corrosion-monitoring techniques were tested: one based on the linear polarization resistance (LPR) method (Corrater[®] type) and the other based on an electrical resistance (ER) measurement (Corrosometer[®] type). An example of an online corrosion-rate monitoring probe is shown in Figure 15 (Haijtink 1986; Tas *et al.* 1987; Debruyn *et al.* 1988, 1989*a*, 1991).



Fig. 15. Direct corrosion-rate monitoring probe (Corrosometer[®] type) (Haijtink 1986).

Experience gained during the operational phase of the in situ *corrosion experiments*

The exploitation of the Type I corrosion experiments did not yield any problems. These corrosion test tubes were implanted horizontally in holes that were drilled into the clay. The drilled holes were about 25 cm larger in diameter than the corrosion test tubes. The clay converged around the tubes shortly after emplacement. It took, on average, about 4 months to reach uniform contact of the clay medium over the entire tube length. This corresponds to an approximate rate for the clay-front movement of about 0.4 m a⁻¹ (Debruyn *et al.* 1986; Van Iseghem *et al.* 1993; Kursten *et al.* 1997; Kursten and Van Iseghem 1998*b*, 1999).

The temperature along the test tubes (measured using thermocouples) remained constant with time at the target temperature (16, 90 or 170° C). For the tubes operated at 90 and 170° C, however, the temperature was not constant over the entire sample section: at the ends of the section, the measured temperature was up to 20° C below the target temperature. This was because the heating elements were not mounted over a sufficient length (Van Iseghem *et al.* 1993; Kursten *et al.* 1997).

The four type I corrosion test tubes were successfully retrieved by overcoring the tubes. In one case (test tube No. 1), however, the overcoring was hindered by to the unexpected presence of freezing pipes (used for the construction of the HADES URL) at about 2 m from the gallery lining. One carbon steel ring got slightly damaged during cutting of the tube (Van Iseghem *et al.* 1993; Kursten *et al.* 1997).

Unexpected operating conditions necessitated the interruption of four Type II corrosion experiments. A malfunction in the water-evacuation system resulted in too high a water level inside the tubes, thereby damaging the heating elements and invalidating the results. An unexpectedly large flux of humidity through the porous filter resulted in the accumulation of liquid at the bottom of the test tubes because the original pumping system was not suited for the observed fluxes. As a result, the various metallic samples had, in almost all cases, been in contact with clay water rather than with a humid clay atmosphere. This caused part of the heating elements to be

immersed in liquid, which overheated the part of the element that was out of the water. This led to the interruption of the first four Type II corrosion experiments twice, and it was decided to redesign the test assembly with a new automated pumping system and a new technique for positioning the samples. Figure 16 shows a part of the Teflon[®] sample holder of the originally designed test tube No. 8 after being exposed to a humid clay atmosphere for 4 years. Owing to the problems described above, the samples suffered severe corrosion, resulting in a partial 'coalescence' of the samples. Therefore, an in-depth investigation and the determination of the average corrosion rate of these samples were considered pointless (Van Iseghem et al. 1993; Kursten et al. 1997; Kursten and Van Iseghem 1998b, 1999).

An interesting spin-off from the operation of the Type II test tubes was that the humidity percolation through the porous filter was in agreement with the calculated value, using actual knowledge of the clay properties. This confirmed the value for the hydraulic conductivity ($K = 3.2 \times 10^{-10}$ m² s⁻¹ MPa⁻¹) proposed at that time (Van Iseghem *et al.* 1993; Kursten *et al.* 1997).

The operation of one of the Type III corrosion experiments (test tube No. 9) was stopped prematurely due to the number of problems it had caused. The electrical resistance heating the inner section of the tube failed several times, probably due to a too low insulation resistance of one of the heating elements or a short circuit of the lower heating elements (Van Iseghem *et al.* 1993; Kursten *et al.* 1997; Kursten and Van Iseghem 1999).

A few problems were encountered during the installation of the second Type III corrosion test tube (test tube No. 10). A first oblique drilling had to be interrupted due to the presence of a freezing pipe at a depth of 4.7 m behind the gallery lining. The drilled hole had to be refilled immediately with clay to limit the mechanical disturbances in the surrounding environment. The second attempt to drill the borehole, at a higher inclination of 10%



Fig. 16. Teflon[®] sample holder of the originally designed Type II corrosion test tube No. 8 after retrieval after exposure to a humid clay atmosphere for 4 years showing, on the left side of the photograph, the corroded carbon steel samples that are 'partially' coalesced (Kursten *et al.* 1997).

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to avoid the freezing pipe, was successful. Test tube No. 10 had a slightly modified design enabling accommodation of more samples in the porous concrete section compared to test tube No. 9. Test tube No. 10 was also equipped with a revised automatic drainage system, which allowed the tube to operate under an inert atmosphere. Two electrical water detectors were fixed on the inside of the tube at different levels. When the water level reached the higher detector, an electrical signal interrupted the helium flow inside the tube and the accumulated water was allowed to flow out into an argon-filled flask until its level reached the lower detector. The system then returned to its normal operating conditions (Kursten *et al.* 1997).

Retrieval of the in situ corrosion experiments

The retrieval of the Type I *in situ* corrosion test tubes was achieved using an 'overcoring technique'. This yielded a clay layer about 15 cm thick around the tube, which enabled analysis of the clay in contact with the samples. The different steps of the overcoring technique are presented in Figure 17

In the first step, and after some dismantling was carried out (disconnecting the electrical wiring and removing the flange), the clay was excavated starting from the access hole up to the stainless steel carrier tube. At the same time, a steel casing was introduced to prevent the clay from collapsing and to provide lining. In a second step, a number of holes of about 12 cm in diameter were drilled along the periphery of the borehole. Hydraulic jacks were used to push a slightly conical jacket through this weakened zone. The conical shape of the jacket made the clay break off easier when the jacket reached the end of the stainless steel carrier tube. Finally, the test tube with the samples surrounded by a clay layer about 15 cm thick could be withdrawn from the borehole. The block was covered with plastic to prevent the clay from drying out.

The test tube was then further dismantled in the surface laboratory. First, the steel jacket was cut away with a cutting torch. After mechanically cutting the clay layer, the clay could easily be removed from the specimens. Because of the compactness of the clay, it could be removed as a whole, allowing accurate recording of the relative positions of the surrounding clay section to each individual metal specimen. After dismantling the tube, all the samples were stored in a glove box under argon to prevent modification of the surface layers before analysis (Debruyn *et al.* 1986; Kursten *et al.* 1997; Kursten and Van Iseghem 1999).

Figure 18 shows a Type I corrosion test tube after retrieval from the URL. The 15 cm-thick clay layer, surrounding the steel carrier tube (loaded with the test samples), was partially removed using mechanical tools. As can be seen in Figure 18a, only the carbon steel samples (right side of the tube) had a corroded appearance.

It was also observed during the overcoring procedure and the retrieval of the ring-shaped samples of the Type I test tubes that the clay exhibited a high degree of plasticity. The clay was not only present underneath the metallic rings but also underneath the Teflon[®] spacers used (Debruyn *et al.* 1989*a*).

Retrieving the metallic samples placed inside the Type II and Type III test tubes was straightforward because these test tubes were designed so that the tests could be interrupted periodically for specimen examination and/or exchange: the Teflon[®] sample holder containing the metallic samples could simply be pulled out from the inside of the test tubes (Debruyn and Tas 1988; Van Iseghem *et al.* 1993; Kursten and Van Iseghem 1999). Figure 19 gives a view of the Teflon[®] holders (with the test samples still mounted inside) of the Type II test tube Nos 5b and 8b after being in contact with a humid clay atmosphere for about 2 years at 90°C and for about 2.5 years at 16°C, respectively.

Analysis methods

The mass losses and average thickness reductions were calculated after chemical cleaning of the metallic samples. The average uniform corrosion rates were determined from the weight lossmeasurements of the metallic coupons according to the guidelines of ASTM procedure G1-90. The reported corrosion rates were averaged over the whole exposure period. The surface that was taken into account for these calculations is the entire surface of the samples. For the ring-shaped samples (Type I test tubes), this means that not only the outer, but also the inner, surface of the samples was considered because signs of corrosion due to clay and moisture infiltration between the samples and the insulating Teflon[®] linings were noticed on the inside of the carbon steel rings (Cornélis and Van Iseghem 1993; Kursten et al. 1997).

Various surface analysis techniques were used to characterize the composition of the corrosion product layers formed on the samples and the morphology of the underlying metallic surfaces. Typically, stereomicroscopy with magnifications of up to \times 50 was used to survey the surface of chemically cleaned samples and to select, whenever the metal was pitted, some of the pits that appeared to be among the deepest. In these cases, optical microscopy was used to measure the depth of the selected pits, in accordance with ASTM procedure G46-76 (analysis of a large number of embedded and polished cross-sections) by first focusing on the sample surface at the lip of the pit and subsequently focusing on the bottom of the pit. The difference between the two readings



Removing the flange (after disconnecting all electrical wiring from heating elements, measuring devices, etc.).



Introducing a steel casing to prevent the clay from collapsing and to provide lining.



Excavating clay from the access hole up to the steel carrier tube.



Drilling small holes at the periphery of the carrier tube. A hydraulic jack was used to push a slightly conical jacket through the weakened clay.



Front view of the conical jacket.



Withdrawing the steel casing containing the specimen section of the test tube embedded in a layer of clay.

Fig. 17. Retrieval procedure of the Type I corrosion experiments in the HADES URL (Kursten and Van Iseghem 1998b).

was then used to calculate the pit depth. Profilometry was only used on a few carbon steel samples. Metallography, scanning electron microscopy (SEM), Auger analysis, electron microprobe analysis (EMPA) and X-ray diffraction analysis (XRD) were used on the unetched polished cross-section of ultrasonically cleaned specimens (Cornélis and Van Iseghem 1993).

Experimental results from the *in situ* corrosion experiments

In situ characterization of the underground clay environment

Monitoring of the pH and Eh in the vicinity of the Type I test tube No. 4 (16°C) started at the end of

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Fig. 18. Type I *in situ* corrosion test tube No. 1 (direct exposure to clay for 5.7 years, 170° C) after mechanically breaking open the clay layer: (**a**) section containing the metallic samples and (**b**) section containing the wasteform samples (Kursten *et al.* 1997).

1986, approximately 1 year after the installation of the test tube in the clay formation. Valid pH and Eh values could be recorded as soon as a close contact between the test tube and the surrounding clav was established. The evolution of the pH and Eh for test tube No. 4 is given in Figure 20. The pH was found to evolve relatively rapidly from initial acidic values, corresponding with aerated clay conditions, to alkaline values. A value of 8.2 was reached after only 1 month of exposure and a stable value of about 9.2 was reached after a further 3 months of exposure. From Figure 20, it can also be observed that it only took about 1 month for the redox potential to stabilize at a value typical for reducing conditions of the undisturbed clay formation (-300 mV v. the standard hydrogen electrode (SHE) scale). These results clearly showed that the clay has a high capacity to recover from

the disturbances caused by the drilling operation (Debruyn *et al.* 1988, 1989*a*, *b*, 1991; Debruyn and Tas 1988).

After relatively long exposure times (\geq 1.5 years), the pH and Eh started to drift from their stable values, and reliable values could no longer be measured. This is illustrated in Figure 21. This failure was believed to be due to a progressive poisoning effect caused by the reducing species present in the clay: the Ag⁺ ions from AgCl were being reduced to form Ag, which resulted in a final destruction of the reference electrode system. At elevated temperatures (90 and 170°C), the disintegration process of the reference electrode seemed to occur even faster. Drifting of the measured values started much earlier in the exposure period and was more accentuated than at 16°C. This is illustrated in Figure 22 (Debruyn *et al.* 1991).



Fig. 19. Teflon[®] sample holder of the Type II *in situ* corrosion test tubes after exposure to a reducing humid clay atmosphere: (a) exposure for 2 years at 90°C, test tube No. 5b; (b) exposure for 2.5 years at 16°C, test tube No. 8b (Van Iseghem *et al.* 1999).



Fig. 20. Evolution of (a) pH and (b) Eh for test tube No. 4 (16°C). Measuring period: October 1986–April 1988 (Debruyn *et al.* 1991).

In situ corrosion potential measurements

Figure 23 shows the evolution of the corrosion potential (E_{CORR}) of carbon steel exposed to clay at 16°C for two types of pretreatment: as-received and polished. Initially, values between +100 and +200 mV (v. SHE) were measured, indicating that

the samples were in contact with an oxidized clay environment. After 2 weeks, a steep potential drop proved that the clay became anaerobic and recovered from the drilling disturbances. All samples then evolved towards an equilibrium value of around -500 mV (v. SHE). The evolution of E_{CORR} towards negative stable values was faster for the



Fig. 21. Evolution of (a) pH and (b) Eh for test tube No. 4 (16°C). Measuring period: October 1986–March 1989 (Debruyn *et al.* 1991).



Fig. 22. Evolution of (a) pH and (b) Eh for test tube No. 1 (170°C). Measuring period: June 1988–March 1989 (Debruyn *et al.* 1991).

polished samples compared to the as-received samples (Debruyn *et al.* 1991).

Online corrosion-rate monitoring

The LPR probes installed directly into the clay yielded unstable and unrealistic corrosion-rate



Fig. 23. Evolution of the corrosion potential, E_{CORR} , of as-received and polished carbon steel mounted on test tube No. 4 (16°C) (Debruyn *et al.* 1990*a*, *b*).

readings. The actual corrosion rates were too low for this technique to be viable, particularly under the complex conditions of a solid clay environment. The ER probes buried in the clay, conversely, yielded highly stable signals (Fig. 24). Even if the initial level of the signal was considered to correspond with corrosion, which may have taken place under the oxidizing conditions prevailing immediately after probe introduction, the subsequent evolution of the signals indicated that the overall corrosion rates were extremely low, both for cast iron and for Hastelloy C-4. These recorded values were well below the detection limits generally accepted for this technique and the probes concerned. However, given the stable exposure conditions, the long exposure times and the stability of the control voltages, the stable signals were believed to indeed correspond with extremely low material degradation rates. For cast iron, the integrated metal loss amounted to 0.19 µm. For Hastelloy C-4, the in situ measured accumulated metal loss evolved from 0.04 to 0.06 µm over a measuring period of 290 days. This means that Hastelloy C-4 is not completely stable in the clay environment but continued to corrode at an extremely low rate (Debruyn et al. 1989a, b, c, 1991).

Analysis of the clay samples

The solid clay contacting the overcored type I test tubes could easily be removed from the metallic samples. As explained above, the compactness of the clay made it possible to remove it as a whole and



Fig. 24. Metal losses as a function of exposure time, measured with ER probes, for (a) cast iron and (b) Hastelloy C-4 (Debruyn *et al.* 1989*c*).

accurately record the relative positions of the surrounding clay section for each individual metal specimen. From each such clay section, cylindrical samples were taken by hand drilling. Subsequently, each cylinder was subdivided into thin clay slices by means of a microtomy technique. The thickness of each slice was 0.2 mm. The complete sampling procedure was carried out in a glove box under an argon atmosphere to minimize the disturbance of the samples. Each sample (slice) was chemically analysed by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES): after leaching, the elements present were excited in an ICP and their emitted spectral lines were interpreted by AES. This technique allowed determination of the concentration profiles of alloy elements not present in the unaffected clay or elements present in a noticeable concentration above the clay background. This information provides a qualitative idea of the migration distances and the diffusion rates of corrosion products in the surrounding clay. The surrounding clay was not affected by the introduction of corrosion-resistant alloy samples such as Hastelloy C-4 and Ti/0.2Pd. The situation, however, was different for carbon steel: the corrosion products of the carbon steel samples migrated from the steel surface into the clay at an average rate of 0.3 mm a^{-1} . From this result, a migration coefficient of the corrosion products of 1.6×10^{-11} cm² s⁻¹ was calculated (Debruyn et al. 1989a, b, 1991).

Analysis of the metallic samples

Visual inspection. A preliminary visual inspection of the exposed metallic samples (after retrieval of the test tubes) revealed that only carbon steel showed severe signs of corrosion attack after being in contact with any of the three test conditions (i.e. direct contact with the Boom Clay, humid clay atmosphere or concrete-saturated humid clay atmosphere). From Figures 25 and 26, it can clearly be seen that only the carbon steel samples showed a rust-brown colour, which is typical for corrosion products of iron, while all other samples remained fairly unaltered.

Corrosion-allowance materials. Table 11 summarizes the average uniform corrosion rates and the maximum pit depths of carbon steel, loaded on the Type I (direct contact with clay), Type II (humid clay atmosphere) and Type III (concrete-saturated clay atmosphere + direct contact with clay) corrosion test tubes. Carbon steel exhibited significant corrosion in direct contact with clay, and its uniform corrosion rate increased with increasing temperature from 1.8 μ m a⁻¹ at 16°C to 8.6 μ m a⁻¹ at 170°C (test duration of 4.7 years). The uniform corrosion rate also decreased with exposure time from 7.7 μ m a⁻¹ (test duration of 1.7 years) to 4.6 μ m a⁻¹ (test duration of 7 years) at 90°C.

Carbon steel also exhibited severe signs of pitting corrosion after interaction with Boom Clay, with



Fig. 25. Line-up of the different types of ring-shaped metallic samples loaded onto test tube No. 3 after direct exposure to Boom Clay for 7.5 years at 90°C (Kursten *et al.* 1997).

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Fig. 26. Line-up of the different types of square metallic samples loaded on test tube No. 8b after exposure to a humid clay atmosphere for 2.5 years at 16°C (Kursten and Van Iseghem 1998*c*).

maximum pit depths detected in the parent material of up to $240 \,\mu\text{m}$ after 2 years at 90°C . The weld material of carbon steel was more susceptible to pitting corrosion than the parent material. This

localized form of attack was even more pronounced in the presence of a γ -radiation field (400 Gy h⁻¹): thickness reductions of *c*. 2200 µm in the heat-affected zone of the weld were observed after

Corrosion medium	Temperature (°C)	Exposure period (years)	γ dose rate (Gy a ⁻¹)	Surface finish	v_{CORR}^{*} (µm a ⁻¹)	$d_{ m MAX}^{\dagger}\left(\mu { m m} ight)$
Direct contact with Boom Clay (Type I)	170 90 90 16 16 [‡] 80 [§]	4.7 1.7 7.0 4.7 3.0 5.0	0 0 0 0 400	as as as as as p as as	8.59 7.68 4.65 1.81 8.57 5.47 3.8 20.3	n.d. 240 (parent material) 90 (parent material) 130 (weld region) 100–120 (parent material) 260 45 150 (parent material)
Humid clay atmosphere (Type II) Concrete-saturated clay atmosphere (Type III)	90 16 90 16	2.0 2.5 2.0 2.5	0 0 0 0	as p cc as p cc as as p	9.03 3.24 8.09 5.13 0.40 5.18 0.73 9.48 1.31	$ \begin{array}{c} 2170 \text{ (weld region)} \\ 180 \\ 30 \\ 245/105^{\parallel} \\ 195 \\ 75 \\ 245/65^{\parallel} \\ 60 \\ 235 \\ 50 \\ \end{array} $

Table 11. Average corrosion rates (calculated from weight-loss measurements) and maximum pit depths of carbon steel exposed to different underground clay environments (Kursten et al. 2004a, b, c)

n.d., not determined; as, samples tested in the 'as-received' condition (no surface treatment was applied); p, samples tested in the 'polished' conditions; cc, samples with an artificial crevice.

*v_{CORR}, average corrosion rate.

 $^{\dagger}d_{MAX}$, maximum pit depth.

*Samples mounted on the outside of a Type III corrosion test tube.

[§]Results originating from the CERBERUS experiment.

¹¹Maximum pit depth measured at the edge of the crevice/maximum pit depth measured inside the crevice.



Fig. 27. Optical micrograph of the corrosion attack of a carbon steel weld exposed to clay for 5 years at 80°C and a γ -radiation dose rate of 400 Gy h⁻¹ (Noynaert 2000; Kursten *et al.* 2004*a*, *b*, *c*; Kursten and Druyts 2006).

direct exposure to Boom Clay for 5 years at 80°C (Fig. 27). In addition, although it was generally assumed that a humid clay atmosphere and a concrete-saturated humid clay atmosphere would be less aggressive than direct exposure to Boom Clay, no noticeable difference in the degree of corrosion attack was observed (Kursten *et al.* 1997, 2004*a*, *b*, *c*; Kursten and Van Iseghem 1998*a*, 1999; Noynaert 2000)

In many cases, optical microscopy revealed the presence of cracks in the oxide layers in the unetched, polished cross-sections of ultrasonically cleaned samples for the test at 170° C (Fig. 28). It was not well understood how these cracks formed. However, whether they had occurred before the *in situ* test (during storage in the laboratory) or during the interaction with the clay, the unprotective nature of the corrosion layers is evident (Cornélis and Van Iseghem 1993; Kursten *et al.* 1997).

Surface analysis of the carbon steel samples (optical microscopy and SEM) revealed that the morphology of the corrosion attack was that of hemispherical pitting. On many occasions, pits had coalesced, resulting in the appearance of general corrosion. Also, the presence of 'secondary' pitting (i.e. the initiation of smaller pits inside already existing pits) was observed, together with intergranular attack at the bottom of the pits (Debruyn *et al.* 1990*a*; Cornélis and Van Iseghem 1993; Kursten *et al.* 1997; Kursten and Van Iseghem 1999). It was believed that the succession of wide pits with abraded edges, giving the surface of the carbon steel samples an appearance of general pitting, was formed by a combination of two effects (Cornélis and Van Iseghem 1993; Kursten *et al.* 1996, 2004*c*; Kursten and Van Iseghem 1999), as follows:

- As oxygen was consumed relatively quickly by the corrosion reactions of the carbon steel samples after closure of the borehole in the URL, and as the steel did not build up an effective protective layer, existing pits may have coalesced, resulting in a rough, coalesced pit appearance of the steel surface. Theoretically, pit coalescence (shallow pits) could occur if the pits were not surrounded by passive regions on the metal surface (Farvaque-Béra and Leistikow 1991).
- Formed pits were eventually covered with corrosion products that restricted the flow of ionic species into or out of the pits. Deposition of corrosion products at the mouth of the pits (due to the lower solubility of corrosion products in the higher pH environment outside the pits) could have inhibited mass transfer. Thus, a pit eventually became a small crevice, thereby rounding off the pit edges. This resulted in a succession of wide and shallow pits (Kruger and Rhyne 1982).

The surface morphology of the corrosion attack appeared to be different according to the test temperature, as illustrated in Figure 29 (Cornélis and Van Iseghem 1993; Kursten *et al.* 1996, 1997, 2004*c*; Kursten and Van Iseghem 1999):

 Samples corroded for 5 years at 16°C (initial clay temperature) and samples corroded for 2 years at



Fig. 28. Unetched polished cross-section of carbon steel after 5 years of exposure to clay at 170°C (Cornélis and Van Iseghem 1993).

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Fig. 29. SEM micrographs of the surface of chemically cleaned carbon steel samples after direct exposure to Boom Clay for (**a**) 5 years at 16° C, (**b**) 2 years at 90°C and (**c**) 5 years at 170°C (Kursten *et al.* 2004*a*, *b*, *c*).

90°C presented a rather similar appearance of general pitting, as shown in Figure 29a and b, respectively. The observations at 16°C revealed maximum pit depths up to 100–200 μ m. The samples tested at 90°C for 2 years showed zones of attack typically extending over 2–3 cm². The maximum depth of this form of localized attack was 240 μ m.

• At 170°C, however, a different surface morphology was observed. Although the surface did present signs of general pitting, it looked more eroded with a succession of wider pits with abraded edges, as illustrated in Figure 29c.

The differences in surface morphology of the carbon steel samples exposed to Boom Clay at various temperatures and for different lengths of time can be explained as follows. During the initial aerobic phase of the experiment, corrosion proceeded predominantly, if not only, by pitting. The rate at which this pitting corrosion occurred was influenced by the test temperature. When oxygen was consumed (i.e. during the subsequent anoxic phase), corrosion proceeded uniformly, thereby displacing the metal surface parallel to itself or even progressively eroding its irregularities.

The similarity in the appearances of the samples corroded for 5 years at 16° C and for 2 years at 90° C could then be explained by the fact that, although

the initial pitting damage would have been higher at 90°C than at 16°C, it was afterwards counterbalanced by slower but longer homogeneous corrosion for the experiment conducted at 16°C. For the test at 170°C, both the influence of the temperature on the kinetics of corrosion and the duration of the experiment will have been responsible for the eroded aspect of the surface (Cornélis and Van Iseghem 1993; Kursten *et al.* 1997, 2004*c*).

To be able to interpret the influence of the solid clay phase on the formation of the corrosion layers, a comparison was made with corrosion layers formed on 'blank' carbon steel samples: that is, samples stored in the laboratory under ambient conditions and for approximately the same length of time. The EMPA micrographs of the cross-section of carbon steel samples exposed to ambient laboratory conditions for 5 years ('blank' sample), and to clay at 16 and 170°C are shown in Figure 30. The corrosion layer formed on the 'blank' carbon steel samples appeared on average to be about 10-20 µm thick. Moreover, the layer was subdivided into three sublayers, of which the middle one had a higher Fe/O ratio compared to the other two. It could have corresponded to a layer that was initially protective - possibly magnetite-containing (Fe₃O₄) - and had cracked, thereby allowing corrosion to proceed further, forming a hematite-type corrosion product (Fe₂O₃). This multilayered structure of the corrosion



Fig. 30. EMPA micrographs of the cross-section of uncleaned carbon steel samples: (**a**) 'blank' sample (i.e. stored in the laboratory under ambient conditions), (**b**) exposed to clay for 5 years at 16° C and (**c**) exposed to clay for 5 years at 170° C (Kursten *et al.* 2004*a*, *b*, *c*).

layer was less obvious after interaction with clay for 5 years at 16°C and had practically disappeared after 5 years at 170°C, as illustrated in Figure 30. In both cases, the corrosion layer was approximately 30-50 µm thick in total. Figure 30b suggests the presence of two layers of iron oxide. Here again, one oxide layer clearly had a higher Fe/O ratio than the other. It could also be seen that this laver was cracked. This again suggested that this layer was probably protective in the beginning but that its rupture had allowed localized corrosion to occur underneath it. Indeed, a rather large pit could be detected on the metallic surface just at the interface of this thin layer. Figure 30c is interesting as it shows the presence of SiO₂, originating from the clay, in the corrosion layer. This corrosion layer was more homogeneous in composition than in the two other cases (Kursten et al. 1996, 1997, 2004c).

Corrosion-resistant materials. The surfaces of the candidate corrosion-resistant materials (stainless steels, Ni-alloys, pure Ti and Ti/0.2Pd) remained unaffected after exposure to any of the three test conditions. This result was consistent with the negligibly small measured mass losses ($<0.1 \ \mu m \ a^{-1}$). The weld material was found to be no more susceptible to corrosion than the parent material (Kursten and Van Iseghem 1998*a*, 1999; Noynaert 2000; Kursten *et al.* 2004*b*, *c*).

Implications of the corrosion studies on the disposal concept

The outcome of the in situ corrosion experiments has contributed to ONDRAF/NIRAS' decision to abandon carbon steel as the reference overpack material in direct contact with the clay environment. The fast growth of pits during the aerobic period, together with the large amounts of hydrogen gas generated during the subsequent anaerobic period, was believed to have had a detrimental impact on the overpack's integrity and the mechanical stability of the clay host rock. Conservative reasoning - a constant pit propagation rate (i.e. no repassivation occurs) and a constant supply of oxygen to the overpack surface - suggested that even maximum pit depths of up to 240 µm over a period of 2 years (as measured in the in situ corrosion experiments at 90°C) could lead to a fast perforation of the 25 mm-thick carbon steel overpack (a thickness that was fixed from an engineering point of view; Van Miegroet 1993) during the aerobic period. At that time, the aerobic period was estimated to last for about 65 years (Atkinson and Marsh 1991; Cornélis and Van Iseghem 1993; Kursten and Van Iseghem 1999; Kursten et al. 2001; Van Iseghem et al. 2003). In addition, numerical modelling studies indicated that for an average uniform corrosion rate of $1 \,\mu\text{m}$ a⁻¹, which is a conservative value that is much lower than those calculated from the *in situ* corrosion experiments, the hydrogen gas generation rate could exceed the rate that the gas is transported away by diffusion. This could lead to a gas pressure build-up that could damage the host rock and form preferential pathways for the migration of radioactive gases (Volckaert and Mallants 2001).

As a result of these findings, ONDRAF/NIRAS preferred stainless steel instead of carbon steel as the overpack material. Stainless steel was subsequently studied in more detail in a laboratory corrosion programme using electrochemical and immersion tests.

At a later stage, the SAFIR-2 concept was abandoned completely and replaced by the supercontainer concept. A review of the SAFIR-2 report by an international team of eight experts revealed possible weaknesses of the SAFIR-2 reference design regarding the practical feasibility of the EBS and the safe transportation of the waste (OECD/NEA) 2003). Thermal expansion of the centralized steel tube, coupled with the radial pressure exerted by the swelling clay backfill, could cause the steel to be highly stressed. This could in turn lead to plastic deformation of the tube and obstruction of the installation of the waste packages. Other uncertainties were related to the difficulty of transport and emplacement of an unshielded overpack within the disposal galleries (Bel et al. 2006). The change of the disposal reference concept was inspired further by the findings of the laboratory corrosion programme (following the *in situ* programme). It was considered that certain types of corrosion, such as localized corrosion, might threaten the integrity of the overpack during the thermal phase. The reasons included the complex and wide spectrum of local chemical conditions and conditions potentially favouring corrosion (Bel et al. 2006).

Conclusions

In any geological disposal concept, waste containment is achieved by applying the so-called 'multibarrier principle'. This involves the use of several engineered and natural (i.e. the host-rock formation) barriers. The metallic container (referred to as an overpack in the current Belgian concept) is one of the most important engineered barriers to prevent the release of radionuclides and other contaminants in concentrations that pose an unacceptable risk for man and the environment. The main threat to the integrity of the overpack is corrosion through contact with groundwater that may be present in the host rock.

The Belgian Nuclear Research Centre (SCK CEN) initiated an extensive corrosion evaluation

Test material	Humid clay atmosphere	Interstitial clay water	Antwerpian groundwater	Direct exposure to clay
Cast iron	60 μm a ⁻¹ (25°C, 75% RH, 2 year exposure) 150 μm a ⁻¹ (50°C, 2 year exposure)	500 μ m a ⁻¹ (25°C, 16 month exposure) 2000 μ m a ⁻¹ (75°C, 16 month exposure)		10–50 μm a^{-1} (RT, 3 year exposure) pits up to 20 μm deep (1 year exposure) pits up to 600 μm deep (60 year exposure) pits up to 700 μm deep (90 year exposure)
Carbon steel	80 μ m a ⁻¹ (50°C, 4 month exposure) <2 μ m a ⁻¹ (150°C, relatively dry)	215 μ m a ⁻¹ (90°C, air, 40 day exposure) 270 μ m a ⁻¹ (90°C, air, 103 Gy h ⁻¹ , 40 day exposure) 150 μ m a ⁻¹ (90°C, Ar, 40 day exposure) 80 μ m a ⁻¹ (90°C, 103 Gy h ⁻¹ , Ar, 40 day exposure) 5 μ m a ⁻¹ (90°C, air, 9 month exposure) 10 μ m a ⁻¹ (90°C, Ar, 9 month exposure)	<1 μm a ⁻¹ (90°C, anoxic)	10–50 µm a ⁻¹ (RT, 3 year exposure)
Chromized steel	22 μm a^{-1} (50°C, 4 month exposure) 9 μm a^{-1} (50°C, 9 month exposure) 4 μm a^{-1} (50°C, 16 month exposure)	enposite)	1.25 μ m a ⁻¹ (49°C, 4 year exposure)	
AISI 304(L), AISI 316(L) UHB904L	0.35–1.9 μ m a ⁻¹ (50°C, 4 month exposure) 0.25–0.8 μ m a ⁻¹ (50°C, 9 month exposure) 0.04–0.2 μ m a ⁻¹ (50°C, 16 month exposure)	0.1 μm a ⁻¹ (25°C, 3 month exposure)	0–0.0125 μm a ⁻¹ (49° C, 4 year exposure)	

Table 12. Summary of corrosion rates of various candidate overpack materials tested in different environments obtained during the screening studies

1803 T, 1803 MoT AISI 430	1.7–4 μ m a ⁻¹ (50°C, 4 month exposure) 1.1–2 μ m a ⁻¹ (50°C, 9 month exposure) 0.35–1.4 μ m a ⁻¹ (50°C, 16 month expsoure) 0.05 μ m a ⁻¹ (300°C, 4 year exposure)	0.2 μm a ⁻¹ (25°C, 3 month exposure)		
Ni-200 Inconel 600(625) Inconel 800 Hastelloy B(C-4)	$0.5-1.7 \ \mu m \ a^{-1} (50^{\circ}C, 4 \ month exposure)$ $0.4-1.4 \ \mu m \ a^{-1} (50^{\circ}C, 9 \ month exposure)$ $0.1-0.95 \ \mu m \ a^{-1} (50^{\circ}C, 16 \ month exposure)$ $0.02 \ \mu m \ a^{-1} (300^{\circ}C)$	0.25 μm a ⁻¹ (90°C, air, 9 month exposure) 0.08 μm a ⁻¹ (90°C, Ar, 9 month exposure)	0.05 μm a ⁻¹ (90°C, Ar, 9 month exposure)	0.01–0.04 μm a ⁻¹ (13°C)
Copper		60 μ m a ⁻¹ (25°C, 3 month exposure)		
Technically pure Ti Ti/0.2Pd Ti6Al4V, Ti5Al2Sn	1.2–2.1 μ m a ⁻¹ (50°C, 4 week exposure) 0.7–1.6 μ m a ⁻¹ (50°C, 4 month exposure) 0.5–1.2 μ m a ⁻¹ (50°C, 9 month exposure) 0.25–0.6 μ m a ⁻¹ (50°C, 16 month exposure) 0.0025 μ m a ⁻¹ (300°C, 4 year exposure)	 0.1 μm a⁻¹ (25°C, 3 month exposure) 0.6 μm a⁻¹ (90°C, air, 9 month exposure) 0.5 μm a⁻¹ (90°C, Ar, 9 month exposure) 	0–0.0125 μm a ⁻¹ (49° C, 4 year exposure) <0.1 μm a ⁻¹ (90°C, Ar, 9 month exposure)	
Technically pure Al AA-5052H-32 AA-6061T-8	9–15 μ m a ⁻¹ (50°C, 4 week exposure) 11–16.5 μ m a ⁻¹ (50°C, 4 month exposure) 5.5–8 μ m a ⁻¹ (50°C, 9 month exposure) 5–7.5 μ m a ⁻¹ (50°C, 16 month exposure)			Complete deterioration of samples (after 0.42 years of exposure at 300°C)

RH, relative humidity; RT, room temperature.

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programme of various candidate overpack materials and construction materials of galleries and boreholes in the mid-1970s. This programme received the financial support of ONDRAF/NIRAS and the EC.

A stepwise approach was adopted, consisting of: (1) screening studies; (2) detailed studies; and (3) demonstration tests. In the first stage, screening studies were performed on a large number of metallic materials, including cast iron, carbon steel, stainless steel, copper, and Al-, Ni- and Ti-alloys. These studies included accelerated tests, as well as exposure tests, carried out in the laboratory in autoclaves or in a surface clay quarry at Terhaegen. The main aim of these tests was to propose a first selection of the most promising candidate overpack materials. Table 12 gives an overview of the main findings gained during the screening studies. Afterwards, more detailed studies under specifically selected conditions were carried out on this limited selection of metals and alloys. The detailed studies involved in situ experiments and laboratory experiments. The laboratory experiments included electrochemical experiments, immersion tests and specific experiments investigating stress corrosion cracking susceptibility. These detailed studies were aimed at investigating the influence of several parameters such as temperature, type of backfill (Boom Clay or bentonite), presence of aggressive species (Cl-, SO_4^{2-} or $S_2O_3^{2-}$), oxygen content (oxic v. anoxic conditions), presence of a γ -radiation field and influence of radiolysis products. Simultaneously, tests were developed to demonstrate (on a large scale) the feasibility of constructing a DGR and to confirm the corrosion rates and phenomena measured and observed in the previous in situ and laboratory experiments.

The HADES URL has played a crucial role in the corrosion programme because it enabled experiments to be conducted under conditions that were as close as possible to 'real' disposal conditions, which are very difficult (if not impossible) to simulate in the laboratory. These experiments were conceived based on the SAFIR-2 design (the reference design until about 2004). This design placed the metallic overpack in contact with a clay-based backfill material, whose porewater would be altered in time by the ingress of the Boom Clay constituents and which has a pH of between 8.5 and 9.5. The in situ corrosion experiments basically consisted of placing metallic coupons on the outside or inside of a steel support tube, heated from the inside, which was afterwards installed in the underground clay formation. The rationale at that time was that the lifetime of the overpack could be predicted by extrapolating the uniform thickness reduction, which was calculated from the medium-term in situ tests (maximum duration of 7.5 years) to periods of up to a few thousand years. Three

test set-ups were developed to simulate the different environments that were likely to develop in the course of the DGR in clay. The corrosion experiments placed the samples either in 'direct contact with clay' (horizontal, Type I), in contact with a 'humid clay atmosphere' (vertical, Type II) or in contact with a 'concrete-saturated clay atmosphere' (oblique, Type III). The experiments were conducted at three different temperatures: 16, 90 and 170°C. A total of 12 *in situ* corrosion experiments were installed in the HADES URL between 1985 and 1994: four Type I, six Type II and two Type III corrosion experiments.

The main outcomes of the *in situ* corrosion experiments can be summarized as follows:

- The expertise gained from these 'first-generation' *in situ* tests greatly benefitted the *in situ* tests that were later developed and installed in the HADES URL.
- The *in situ* experiments provided valuable information about the behaviour of the Boom Clay host formation that would have been difficult to obtain without testing in the HADES URL:
 - the clay showed a high capacity to recover from the disturbances caused by the drilling operation – it took about 4 months for the pH and Eh to return to the values of undisturbed clay;
 - the clay exhibited a high degree of plasticity it took, on average, around 4 months for the clay to converge around the test tubes after emplacement; and
 - the value of the hydraulic conductivity of the Boom Clay ($K = 3.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ MPa⁻¹), previously determined through laboratory testing, was confirmed in the *in situ* experiments.
- The materials known as 'corrosion-resistant' (stainless steels, and Ni- and Ti-alloys) remained intact after interaction with the underground clay environment. This was found to be consistent with the negligible corrosion rates measured ($<0.1 \ \mu m \ a^{-1}$).
- Carbon steel (corrosion-allowance material) displayed both general and pitting corrosion. Carbon steel exhibited significant uniform corrosion rates that seemed to decrease with exposure time: from 7.7 μ m a⁻¹ (test duration of 1.7 years) to 4.6 μ m a⁻¹ (test duration of 7 years) at 90°C. The uniform corrosion rates also seemed to increase with increasing temperature: from 1.8 μ m a⁻¹ at 16°C to 8.6 μ m a⁻¹ at 170°C. Carbon steel also exhibited severe signs of pitting corrosion, after direct exposure to Boom Clay, with maximum pit depths detected in the parent material of up to 240 μ m after 2 years at 90°C. This localized form of attack was even more pronounced in the presence of a

 γ -radiation field (400 Gy h⁻¹): a thickness reduction of about 2.2 mm in the weld region was observed after direct exposure to Boom Clay for 5 years at 80°C.

 The outcome of the *in situ* corrosion experiments has contributed to ONDRAF/NIRAS' decision to replace carbon steel by stainless steel as the reference overpack material (SAFIR-2 concept, i.e. contact with a clayey environment).

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The corrosion programme on various candidate overpack materials and construction materials of galleries and boreholes considered in the final disposal of vitrified HLW and SF was initiated by the Belgian Nuclear Research Centre (SCK CEN) in the mid-1970s. Later, these studies fell under the supervision of the Belgian radioactive waste management organization (ONDRAF/NIRAS).

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Author contributions BK: writing – original draft (lead); SC: conceptualization (supporting); VDS: conceptualization (supporting); RG: writing – review & editing (supporting).

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