



ELSEVIER

Journal of Nuclear Materials 298 (2001) 86–94

Journal of
nuclear
materials

www.elsevier.com/locate/jnucmat

In situ testing of the chemical durability of vitrified high-level waste in a Boom Clay formation in Belgium: discussion of recent data and concept of a new test

Pierre Van Iseghem ^{a,*}, Elie Valcke ^a, Alexander Lodding ^b

^a Waste and Disposal Department, SCK·CEN, Boeretang 200, B-2400 Mol, Belgium

^b Chalmers University of Technology, SE-41296 Gothenburg, Sweden

Abstract

SCK·CEN has been conducting in situ experimental programmes on candidate high-level waste (HLW) glasses, as part of a global approach to evaluate the long-term chemical durability of the HLW glasses. The in situ tests are conducted in the underground research facility high activity disposal experimental site (HADES), located in the Boom Clay at 223 m below the SCK·CEN site. We briefly present the test concepts for three in situ tests: a first type of corrosion test, tests as part of the Control Experiment with Radiation of the BELgian Repository for Underground Storage (CERBERUS) test (involving γ -radiation sources), and the CORrosion of Active gLass in Underground Storage condition (CORALUS) test, that involves both γ -sources and glass samples doped with α -radionuclides (Np, Pu, Am). The glasses are corroded slightly less compared with the first in situ tests (where no γ -radiation was present). By using mass loss data and an extensive analysis of the reaction layer formed on top of the glasses, we managed to identify the main interaction processes: matrix dissolution and selective leaching. The four glasses studied reveal significant differences in dissolution behaviour. We further discuss the status of the CORALUS in situ corrosion test, which is in its first phase. An inactive CORALUS tube has been prepared and is presently in operation. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Belgium is conducting research and development to investigate and demonstrate the safe disposal of conditioned long-lived, medium-level and high-level radioactive waste in the Boom Clay formation underneath the SCK·CEN site. The studies involve performance assessment calculations and laboratory studies on the near and far field phenomena, and on the behaviour of waste packages. In complement to this, in situ experiments are being conducted in the underground research facility high activity disposal experimental site (HADES), constructed at a depth of 223 m in the Boom Clay formation, as a means to confirm the applicability of the data

from the laboratory tests and of the predictions by the modelling studies. An overview of the various types of in situ tests is given in [1].

This paper focuses on the in situ test programme on vitrified high-level waste (HLW). We will review the different types of in situ tests carried out on HLW glasses, and see how their concept evolved since the early operation of the underground laboratory until now. This paper presents an update of an earlier paper [2].

The in situ tests on HLW glasses constitute an important but not the only approach in studying the long-term interaction between HLW glasses and the geological disposal environment. We also conduct laboratory tests which conclude about the basic interaction mechanisms and the release processes for specific radionuclides of interest. These experimental programmes are complemented with geochemical modelling to explain or predict the effect of e.g., secondary phase formation on the glass dissolution. Mathematical modelling needs to

* Corresponding author. Tel.: +32-14 333 135; fax: +32-14 323 553.

E-mail address: pviseghe@sckcen.be (P. Van Iseghem).

provide means to extrapolate the glass dissolution over long periods of time. In situ testing is expected to provide a confirmation in the real environment of the applicability of the data obtained in the laboratory, and by doing so to enhance the confidence in the geological disposal concept.

2. Description of the in situ tests on HLW glasses

Three types of in situ corrosion tests have been designed, bringing the glass samples in direct contact with Boom Clay. Emphasis has been on this interaction because this is the ultimate environment that the HLW glass will contact upon degradation, and also because we know it to be the most aggressive clay medium for glass degradation [3]. The first in situ test was conceived in 1983, the second one (Control Experiment with Radiation of the BELgian Repository for Underground Storage (CERBERUS)) in 1988, and the third one (CORrosion of Active gLAss in Underground Storage condition (CORALUS)) in 1997. Full descriptions of the test concepts and exploitation for the first two tests are given in [4–6]. The concept of the third test is given in [7]. A design of the CERBERUS and CORALUS in situ tests is shown in Fig. 1.

The first type of in situ test involved the direct exposure of HLW glass samples to Boom Clay at a specified temperature and time. This was done by ‘simply’

loading glass samples on large steel tubes which were inserted in the Boom Clay surrounding the underground laboratory, and heating the tubes via internal heating elements. The duration of contact between the glass samples and the clay was monitored, and the tubes were retrieved via overcoring after the fixed duration. We performed tests at 16°C, 90°C and 170°C, for four durations in total (2–7.5 yr). A special feature was that a few glass samples were added which were doped with ¹³⁴Cs, ⁹⁰Sr and ²³⁹Pu, and that we succeeded to recover some solution from the Boom Clay environment via centrifugation/filtration, which could be used for analysis.

The second type of in situ test added the parameter of a γ -radiation field (CERBERUS). This in situ test was meant to study the effects on the near field in an argillaceous environment of a Cogema HLW canister after 50-years cooling time. ⁶⁰Co sources and a heating system generated the conditions in which the Boom Clay was studied. We took the opportunity to place non-radioactive HLW glass samples in the vicinity of the ⁶⁰Co sources, so that the glasses interacted with the natural Boom Clay in the presence of the γ -radiation field. The glass samples were exposed to the Boom Clay for 5 years at a temperature between 80°C and 85°C.

The third in situ test is called CORALUS, and has entered its experimental phase. The CORALUS test adds to the CERBERUS test α -activity in the glass samples (about 0.85 wt% of ²³⁷NpO₂, ^{238–242}PuO₂ or

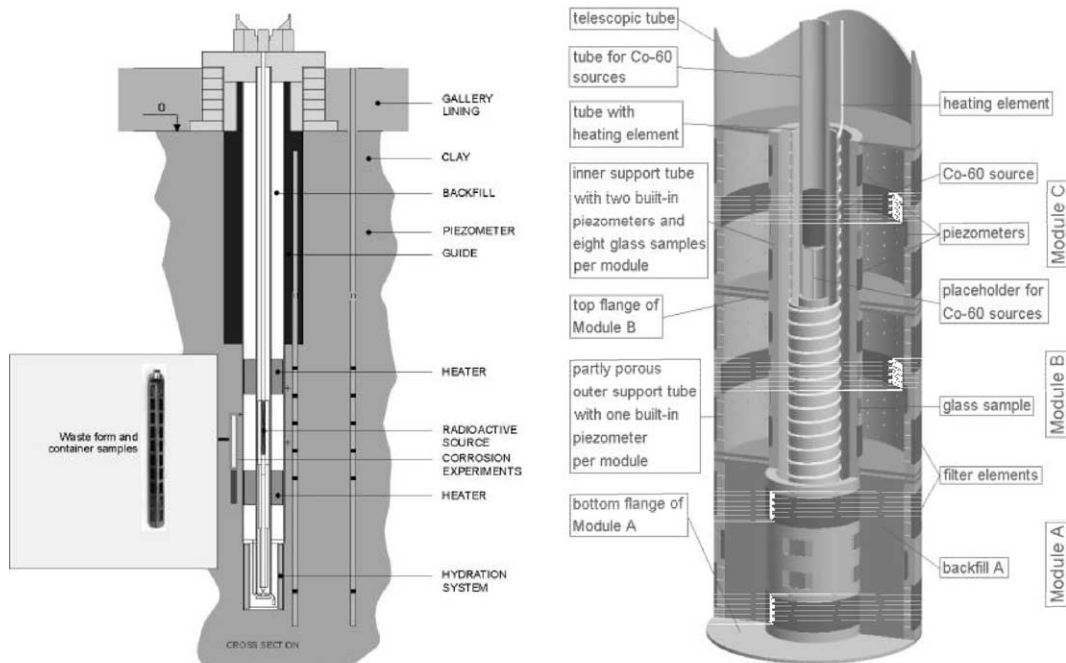


Fig. 1. Design of the CERBERUS (left) and CORALUS (right) in situ tests.

$^{241}\text{Am}_2\text{O}_3$), the presence of different reacting environments (two candidate backfills and Boom Clay), and the monitoring of the gas generated close to the radiation sources. The γ -doses to which the glass samples will be submitted are roughly the same as during the CERBERUS test. The dose rate at the interface glass – clay will range from 240 to 130 Gy/h during a four-year duration of the CORALUS test. This corresponds to the dose rate at the outside of the Cogema glass canister after approximately 100-years cooling time. This project is carried out in co-operation with CEA Valrhô (preparation of the doped SON68 glass) and GRS Braunschweig (monitoring of the gas formation and laboratory investigation of the gas production in the backfill materials).

Most of these in situ tests were or will be performed at 90°C (or slightly below in case of CERBERUS). This is in fact an accidental situation that refers to the initial period after disposal, i.e., supposing the container would fail. HLW glass is poured into a stainless steel canister, and an additional metallic container would provide isolation during the thermal phase of the HLW glass. Other in situ corrosion tests refer to more realistic conditions of temperature. In the first in situ test we had one tube operated at ambient temperature at 220 m depth (16°C). In the new CORALUS test we include a test at 30°C, without γ -radiation field. Both situations correspond with long-time situations. 30°C is the temperature at the interface between the HLW package and the near field after failure of the container after some 500 years (according to the normal evolution scenario). One should of course be aware that it is quite impossible to elaborate a large experimental matrix (different temperatures, various durations) in our in situ tests.

Whereas as much as nine different reference HLW glasses, one reference HLW glass-ceramic and four reference silicate glasses for α -waste immobilization were investigated in the first in situ test [4], the number of different glass compositions was reduced to four in the CERBERUS test (i.e., the borosilicate glasses R7T7 SON68 and PAMELA SM513 and SM527, and the silicate glass WG124 [8]. The chemical compositions are listed in Table 1. All HLW glass samples studied here

were reference glass samples prepared in laboratory conditions. In the CORALUS test we consider only the R7T7 SON68 glass, which is the main HLW glass for Belgium. Other materials had been loaded on the corrosion tubes as well. Bitumen and cement waste form samples and metallic container samples (various carbon steels, stainless steels, Ni- and Ti-alloys) were present on the first and second type in situ test [4,5].

The chemical degradation of the glass samples was evaluated by their mass loss measurement, and with an extensive surface analysis programme. We used electron microscopy and secondary ion mass spectroscopy (SIMS) profiling. This had to compensate the lack of solution data – it was not realistic to obtain data for glass matrix elements release into the interstitial solution, if any solution could even be taken. Based on our present experience we will attempt to analyse radionuclide releases into the interstitial solution in the CORALUS test, and we will determine the migration profiles for the radionuclides.

3. Glass corrosion in the CERBERUS in situ test

The mean values of the mass losses of the glasses are plotted together with those from the previous in situ corrosion tests [4,5] in Fig. 2. The mass losses were recorded after cleaning the glass samples with a water spray. This way sorbed clay and other loose deposits or reaction layers are removed. We summarize the results from electron microscopic analysis in Table 2. The cross-section of one sample of each glass (four samples per glass composition were inserted in the CERBERUS test) was analysed by X-ray mapping, and the outer surface of another part of this sample was analysed by scanning electron analysis coupled with electron diffraction analysis (SEM-EDS). Some observations by SEM are shown in Fig. 3. A third fraction of the sample used for electron microscopic analysis was submitted to SIMS profiling. Because some of the reaction layers were several hundreds of μm thick (see Table 2), it was difficult to perform SIMS profiling in the standard way [9] i.e., by

Table 1
Main constituents of the glasses investigated in the CERBERUS in situ test (in wt%)

	SON68	SM513	SM527	WG124
SiO ₂	45.48	52.15	38.75	60.7
B ₂ O ₃	14.02	13.08	21.70	0
Na ₂ O + Li ₂ O	11.84	13.23	11.74	3.6
Al ₂ O ₃	4.91	3.59	19.96	2.9
CaO + MgO	4.04	6.59	4.01	7.0
TiO ₂	0	4.54	1.55	1.1
Fe ₂ O ₃	2.91	1.67	0.7	12.5
Fission product oxides	13.38	4.46	1.58	Not relevant
Balance	3.42	0.69	0.01	12.4

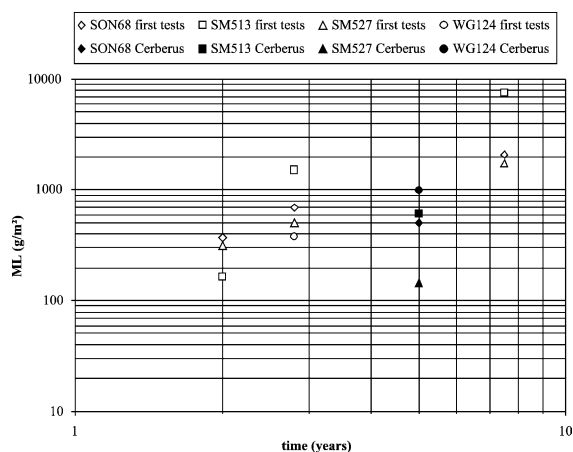


Fig. 2. Mass losses for the different waste glasses after interaction with Boom Clay during the first in situ test (no γ -radiation) and the CERBERUS in situ test.

head-on sputtering through the reaction layers from the surface to bulk glass. For relatively thick and/or brittle layers, a step-scan profiling routine was therefore applied. A discussion of the procedure applied for SIMS analysis and of the data is given in [10]. Complete data and analyses on the waste form samples corroded in the CERBERUS test are given in [11].

The mass losses for the reference HLW glasses are from 2 to 5 times smaller than when no γ -radiation field is present – see Fig. 2. This observation is based on interpolation of the results from the previous in situ tests for 5-years duration. The mass losses for the WG124 glass are not affected by the γ -radiation field. It may be clear that there is no clear-cut effect of the γ -radiation on the mass loss, considering the different effects for the different glasses. We also must be careful in concluding, because the amount of mass loss data is quite small. The reduced pH of the interstitial clay solution due to the radiation (7.2 instead of 8.2) might be one explanation for a slightly lower dissolution, though the literature does not offer a single indication [12,13]. Another factor affecting the average reduction of the mass losses in the radiation field might be the lower temperature: 80–85°C in the CERBERUS test, 90°C in the earlier in situ test. We think that this might contribute for a reduction by up to a factor of 2. Our results from the CERBERUS in situ corrosion test agree with earlier laboratory investigations carried out in Boom Clay slurries, where we also concluded a slight reduction of the glass dissolution upon γ -irradiation, as well as a slight reduction of the solution pH [14]. The pH decrease upon irradiation is due to the oxidation of the pyrite present in natural Boom Clay. Note that the redox potential E_h in the Boom Clay interacting with

Table 2
Information on the reaction layers formed during the CERBERUS corrosion test

Glass	Cross-section	Analysis (EPMA X-ray)	Outer surface analysis (SEM-EDS)
SON68	~ 200 μm thick layer	Relatively enriched in Al and Si, reduced in Ca, Na Influx of K, Mg from clay Between precipitate layer and ‘gel’ layer, another layer is seen (decreased in Si, Al, Ca) (Al, Si, Mg, Fe, K) precipitates on top of layer	(Zn, S) and (Zr, U, Ca, Cr)-rich spots on top of the gel layer No EDS analysis of gel layer
SM513	~ 350 μm thick layer	Relatively enriched in Ti and Al, \pm stable in Si and Fe Reduced in Na, Ca, Mg Influx of K from clay Ca together with S in layer; (Ti, Si, Fe) precipitates	(Si, Al, K, Fe)-rich precipitate layer (Ti, S, Ca)-rich spots, and Ti-rich, long minerals on top of reaction layer No EDS analysis of gel layer
SM527	No typical reaction layer	Thin layer (precipitate?) with (K, Mg, Si, Al, Na (!))	Some precipitates seen on top of gel layer; no EDS analysis
WG124	500–600 μm thick layer	Layer has double structure Outer layer: Fe, Al, Mg relatively enriched; Si, K reduced Inner layer: Mg depleted, Si decreased Ca and Na depleted everywhere (Si, Al, Mg, Fe, K, S) precipitates	Various secondary phases observed i.a. SiO_2 minerals, (Ba, Fe, S) compounds



Fig. 3. SEM pictures of the top of the reaction layer of glasses SON68 (left) and WG124 (middle and right) after corrosion in the CERBERUS test. Left we see a Zn, S phase (the white spots), in the middle an SiO_2 phase (middle of the picture) and in the right picture various phases, with high Ba, Fe and S concentration.

the glass specimens remained negative both without and with γ -radiation.

Analysis by electron microscopy reveals the thickness and composition of the reaction layers formed at the interface of the glasses and the Boom Clay, and any secondary phases present on top of these reaction layers at the ‘clay side’. We see *very* thick reaction layers of 200 to 600 μm , but none in case of the high Al_2O_3 containing SM527 glass. This may be compared with the thinner layers, maximum about 100 μm observed in the previous in situ tests, even after 7.5 years duration [4]. We will take up this stronger reaction layer development when discussing the SIMS profiling. SEM–EDS revealed the occurrence of some secondary phases on top of the reaction layers. Table 2 shows that chemical composition of these phases is different for the different glasses. The (pure?) SiO_2 phase observed for WG124 is interesting, but was not seen on the borosilicate HLW reference glasses. We know from the literature that the saturation of the solution for Si is one of the rate determining steps in the glass dissolution [15], and yet we know that Si reaches maximum steady-state concentrations in solution in Boom Clay slurries [3,16]. SiO_2 containing secondary phases therefore are likely to form. It is conceivable that the Si containing secondary phases observed on top of SM513 and WG124 can enhance the glass dissolution, by suppressing the Si saturation [3]. We cannot even exclude that still other secondary phases are present besides those reported. The detection of these phases within the very irregularly shaped outer reaction layers indeed cannot be complete. We also observed a TiO_2 needle-like phase in glass SM513 which was not stable during SEM–EDS analysis. For these reasons we have no arguments to state that these secondary phases might be influenced by the presence of the γ -radiation field.

We present the data for the major glass constituents (Si, Al, B, Na, Ca) and hydrogen from SIMS profiling analyses for the different glasses in Figs. 4(a)–(d). The figures show that a reaction layer several hundreds of μm thick has formed for all glasses except the high alumina glass SM527. The reaction layers consist of

three main sub-layers. A precipitation layer α is seen, which may consist of an outer precipitation layer α_0 and an inner precipitation layer α_1 . Next, a thick depletion (reaction) zone β_0 , and the diffusion and gradient zones β_1 and β_2 are observed. The element profiles were normalized to Al, because it was seen during the SIMS analyses that Al was relatively inert, i.e., its concentration per volume unit remains relatively stable over the whole reaction layer. The diffusion and gradient zones typically see steep decreases of the alkali elements (Li, Na), alkaline earth (Ca) and other easily diffusing ‘mobile’ elements (such as Mo). There is a simultaneous influx from the leachant into the layers of H and to some extent of such mobile elements which are present in the surrounding clay but not in the bulk glass (such as B and Li in the case of WG124). Elements found (as Al) relatively ‘inert’ (i.e., remaining nearly preserved in the layers) particularly comprise tetravalent transition metals such as Zr, Cr, Ti.

The depletion factor for Si in the entire β reaction layer (as relating to bulk glass composition) is between 0.4 and 0.6 for all glasses but SM527, and about 1 for SM527. This means that Si is clearly impoverished in the reaction layer of SM513, SON68 and WG124, but not depleted close to the surface of SM527. Taking into account the nearly complete elimination in B and the alkali metals in the β layer, we would conclude from the SIMS data that the dissolution of the glasses is predominantly selective-substitutional leaching. (Note that congruent dissolution would result in a depletion factor of 0 for all elements.) The corrosion rates for glasses SON68, SM513 and WG124 therefore would decrease with time, because of the important contribution to the kinetics of other processes than matrix dissolution to the kinetics. The thicker reaction layers after the CERBERUS test compared with the earlier in situ tests [4,17] might be due to a larger contribution from diffusion processes. This, amongst several factors might explain the somewhat lower mass losses after the CERBERUS test. As for the high durability shown by SM527, the present data suggest that this glass is corroded via a particularly clear-cut selective-substitutional dissolution.

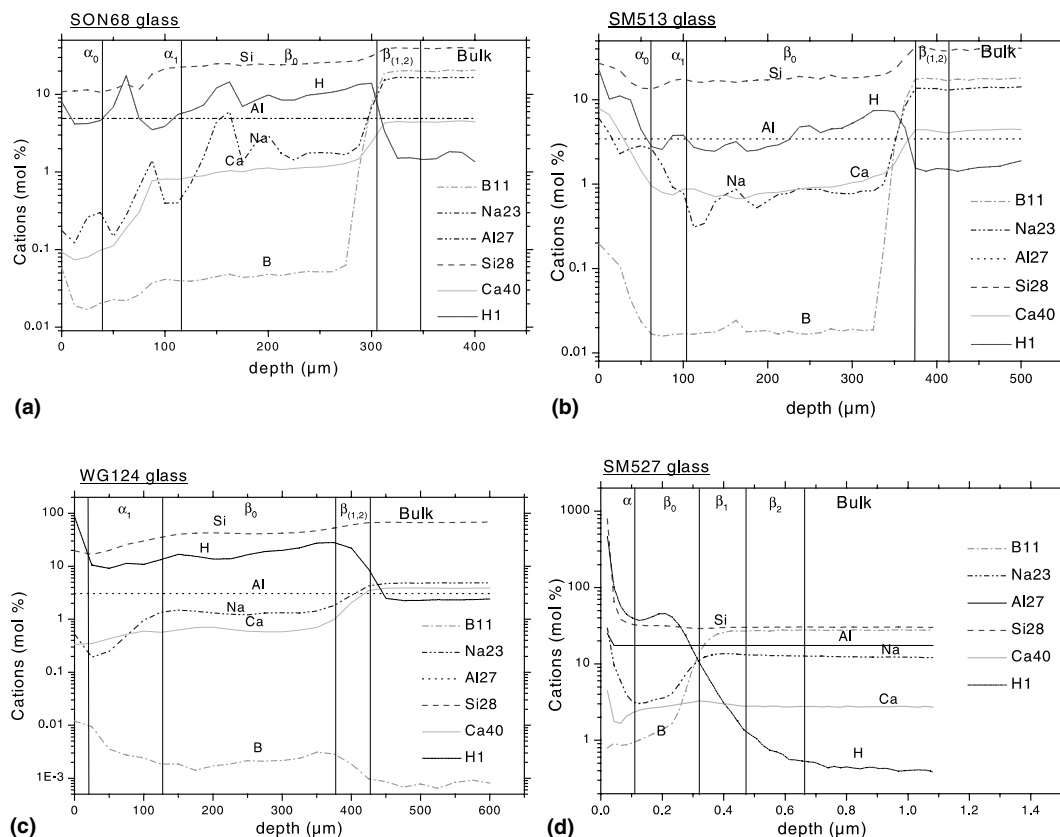


Fig. 4. SIMS profiles for some of the main glass constituents recorded by step-scan for the four waste glasses after five-years interaction at 80–85°C with Boom Clay in the CERBERUS test.

By combining the SIMS data on the reaction layer and the mass loss data (see Table 3) we may attempt to gain a more complete picture of the dissolution process. For the glasses developing a thick reaction layer (SON68, SM513, WG124) the mass losses measured might be due for a considerable part to the leaching processes giving rise to the reaction layer, but not completely. We give an example, stressing that it is not conclusive because we lack precise or sufficient data. Assuming for glasses SON68 and SM513 a density of the $\alpha_1 + \beta$ reaction layer of 40% of the bulk glass density (with the influx elements not being accounted for), 60%

of the original mass of the $\alpha_1 + \beta$ layer would have dissolved from the glass. This would correspond to a depletion depth of some 200 μm (taking the total thickness of the reaction layer from Table 3), which is comparable with the depletion depth based on the mass loss. Thus, the outer glass surface front would not have moved inwards very much. It is difficult to have a precise statement about that anyway, because we do not know the average density of the total reaction layer (including the α and β layers). But we may conclude that these three glasses dissolve via a combination of dissolution and selective-substitutional leaching. Glass SM527 again

Table 3
Characteristics of the reaction layers formed upon in situ interaction with Boom Clay during 5 years at 80–85°C (CERBERUS test)

	SON68	SM513	SM527	WG124
Average depletion depth based on mass loss (μm)	150	236	39	415
Average thickness of $\alpha_1 + \beta$ reaction layer (μm)	320	380	0.5	450
Density of the β_0 layer relative to the bulk glass density (in %) ^a	44	35	57	59
Si depletion factor in the β_0 layer relative to the bulk glass	0.6	0.4	1.1	0.6

^a The density of the layer is calculated by taking into account the concentration of all of the elements in the layer including the influx elements, and the analytical observation that the Al concentration in the β layer is the same as in the glass bulk [10].

appears to behave differently. The net depletion depth measured by mass loss together with the very thin reaction layer suggests that SM527 exhibits some (congruent) dissolution process in addition to the selective leaching as suggested from SIMS analysis.

The combination of the mass loss data and the SIMS profiling therefore provides another picture of the effect of the glass composition on the dissolution behaviour in clay. The first difference between SM527 and the other glasses is the very limited reaction layer formation for SM527, possibly because the glass network is stronger due to the high Al_2O_3 content (Si is not depleted in the reaction layer in the case of SM527). The other three glasses show strong reaction layer formation, with several processes occurring (e.g., network dissolution, selective leaching, ion exchange). In consequence, the much better chemical durability of SM527 in our test (see the mass loss data and the thickness of the reaction layer) can be related for a large part with the smaller extent of the selective leaching processes that generate the reaction layer.

Densities between about 35% and 60% of the bulk glass density suggest that the β_0 reaction layer ‘gel’ should hardly be considered as protective with respect to the leaching of mobile species such as alkali’s and B. Gin et al. [18] argue that the reaction layer formed upon dissolution in clay may be protective, depending on the composition of the clay. It is also to be expected that these reaction layers are becoming thicker with continued interaction with the Boom Clay, possibly becoming less dense even further. We argue that in fact one should add the mass of the main reaction layers to the mass loss as obtained by weight measurement of the glass sample.

4. The CORALUS in situ test

Within the CORALUS project two tubes as shown in Fig. 1 will be loaded in the URF, in the course of 2001, and a third tube in 2002. They will be operated during 2 or 4 years, during which the Np, Pu, or Am doped glass samples will interact with potential backfill materials, in a γ -radiation field, and at a specific temperature (30°C or 90°C). The three modules of each CORALUS test tube are filled with a different backfill material: smectite clay ‘FoCa’ mixed with sand and graphite (60/35/5 wt%), smectite clay FoCa mixed with powdered non-radioactive SON68 glass (95/5 wt%), and dried Boom Clay.

We used, i.a., data from the previous in situ tests for designing the CORALUS test. Considering that the total depth of depletion of the SON68 glass is at maximum ~ 1 mm, we agreed with a thickness for the glass coupons (both active and inactive ones) of 3 mm. The 1 mm total depth of depletion refers to a reacted glass ~ 500 μm thick, based on the mass loss measured in the CERBE-

RUS test, and a reaction layer ~ 400 μm thick measured by SIMS. This assumption might be too conservative, as explained above. The thickness of the backfill materials (35 mm in case of the tests at 30°C, 52 mm in case of the tests at 90°C) was chosen such that we would not expect the radionuclides considered (Np, Pu, Am) to migrate through the backfill towards the outer wall of the CORALUS test. Previous in situ corrosion tests with Pu-doped glass in Boom Clay (90°C, 7.5 yr) showed that the Pu migration distance is limited to a few mm [4]. Within 4 mm from the glass surface we measured a more than 100-fold decrease of the total Pu concentration.

We manufactured and assembled a first fully inactive CORALUS test tube (see Fig. 5), and loaded it in the URF early in 1998. We paid particular attention to the precompaction of the various backfill materials, to the convergence of the surrounding clay onto the test tube in the URF conditions, to the saturation of the backfill materials with clay water, and to testing the procedure to sample solutions containing the generated gases in the inner piezometers. It took three months before the pressure of the surrounding Boom Clay reached its equilibrium value of 6 bar, which is the lithostatic pressure at 4–5 m away from the gallery. We decided to use real clay water sampled in the URF via a piezometer for saturating the CORALUS backfill materials. The complete saturation of the backfills with the clay water took about four months. The sampling of solution for chemical and dissolved gas analysis during the operation of the active CORALUS tubes will be done once a year, for up to 20 ml solution total. Calculations showed that this will not affect the water chemistry close to the glass. We further optimized the procedure for measuring online the pH and E_h of the interstitial solution during the operation of the active CORALUS tests. We also tested the retrieval technique

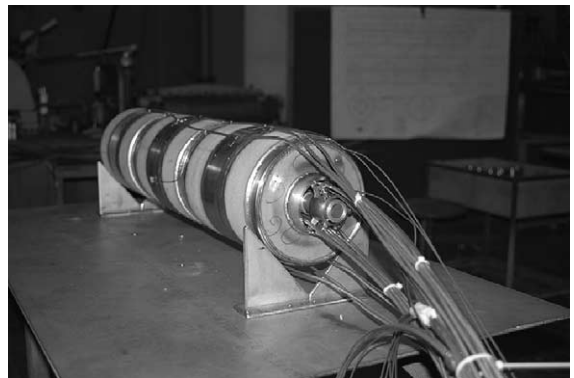


Fig. 5. View of a CORALUS test tube after assembly, and before transport to the underground laboratory. Note that this tube is not foreseen to insert Co-60 sources, and therefore is smaller in diameter than the tubes that will insert Co-60 sources.

of the entire inactive tube, so as to recover the whole backfill material.

5. Discussion

We interpreted the corrosion behaviour of candidate HLW glasses in in situ test conditions by using a combination of mass loss measurements and an extensive surface analysis programme. We were able to roughly identify that the main dissolution mechanisms for the different glasses are network dissolution and selective substitutional leaching. Secondary phase formation was observed on top of some of the glasses. The glasses appear to dissolve a little slower in the presence of the γ -radiation field (CERBERUS test), and at least two relevant effects are reported. The pH of the interstitial Boom Clay water decreases (7.2 instead of 8.2), and the glass corrosion mechanism in general turns more to a diffusion controlled process in the presence of the γ -radiation field.

The in situ corrosion tests running over durations as long as 7.5 years at elevated temperature provided data for glass corrosion over far advanced reaction progress, which are obviously very useful when we attempt to extrapolate to longer time scales. We established from the previous laboratory studies that the Boom Clay provides one of the most corrosive media for the glasses. Our in situ tests are complemented by laboratory tests which are needed to provide data on the basic dissolution processes or the radionuclide release behaviour, and to derive parameters for modelling [3].

The glasses dissolved during the CERBERUS test with a rate between about 10 and 90 $\mu\text{m}/\text{yr}$. Test temperatures between 80°C and 85°C in CERBERUS represent the initial situation after disposal, and therefore cannot be used to estimate the long-term stability of the glasses upon disposal. The data obtained in the first in situ tests at ambient rock temperature (16°C) may be more relevant in this respect. The glass dissolution at 16°C was less than 0.3 $\mu\text{m}/\text{yr}$ in this situation, which illustrates a very important effect of temperature on the glass dissolution in Boom Clay. This demonstrates the need to include low temperature conditions in our future in situ and laboratory investigations.

The in situ tests as conducted are obviously quite inflexible (small amount of experimental conditions possible, long preparation time) and expensive. On the other hand they offered advantages to the current laboratory tests in that they provided natural control of the humidity of the Boom Clay and of the anaerobic environment. This approach might therefore provide an optimal way to study the dissolution behaviour of HLW glasses in integrated conditions, e.g., in the presence of the repository rock (Boom Clay), radiation fields, temperature gradients. The CORALUS in situ test will

provide the most straightforward data in this respect, and will not only provide data on the radionuclide release from the glass, but also on the migration of the radionuclides through the different backfill materials.

The effort spent to generate the data presented in this paper on the glasses exposed to clay in the in situ test was after all quite limited. Indeed the CERBERUS test was designed to study the effect of a γ -radiation field on the near field around a HLW glass package [6], and yet we took the opportunity to install various types of waste form and container samples in the CERBERUS test. Our data on the HLW glass samples demonstrate that very meaningful conclusions could be drawn, even if the CERBERUS test was quite an integrated test.

Acknowledgements

The authors gratefully acknowledge the financial support from NIRAS/ONDRAF and the European Commission for the first in situ corrosion tests and for the corrosion tests on waste forms in the CERBERUS test. They also acknowledge the financial support of the European Commission for the new CORALUS test.

References

- [1] A. Bonne, In situ tests in the HADES facility. In Situ testing of radioactive waste forms and engineered barriers, EUR 15629, 1994.
- [2] P. Van Iseghem, E. Valcke, B. Kursten, A. Lodding, Radioactive Waste Management and Environmental Remediation, ASME, 1999.
- [3] P. Van Iseghem, K. Lemmens, M. Aertsens, M. Put, Interaction between HLW glass and clay: experiments versus model, in: GEOVAL '94, Validation Through Model Testing, OECD, 1995, p. 203.
- [4] B. Kursten, B. Cornélis, S. Labat, P. Van Iseghem, Completion of the corrosion programme in Boom Clay – in situ experiments, EUR 17105, 1997.
- [5] B. Kursten, P. Van Iseghem, In situ corrosion experiments, Final report for 1995–1996, R-3247, 1998.
- [6] R. Beaufays et al., CERBERUS. A demonstration test to study the near-field effects of an HLW canister in an argillaceous formation, EUR 15718, 1994.
- [7] P. Van Iseghem, E. Valcke, N. Godon, N. Jockwer, CORALUS: an integrated in situ corrosion test on α -active glass, in: Scientific Basis for Nuclear Waste Management XXI, Mater. Res. Soc. Symp. Proc., vol. 506, Mater. Res. Soc., 1998, p. 961.
- [8] P. Van Iseghem, D. Hennart, R. De Batist, Characterization of TRUW ceramics in relation to geological disposal in clay, in: Radioactive Waste Products – Suitability for Final Disposal. Jül-Conf-54, 1985, p. 174.
- [9] A. Lodding, P. Van Iseghem, Corrosion of waste glasses in Boom Clay: studies of element concentrations by SIMS, in:

- Scientific Basis for Nuclear Waste Management XIX, Mater. Res. Soc. Symp. Proc., vol. 412, Mater. Res. Soc., 1996, p. 229.
- [10] A. Lodding, P. Van Iseghem, these Proceedings, p. 197.
- [11] L. Noynaert (Ed.), Heat and radiation effects on the near field of a HLW or spent fuel repository in a clay formation (CERBERUS) project, Final Report, EUR 19125, 2000.
- [12] W.A. Ross, et al., Annual Report for 1978 on characterization of high-level waste glasses, PNL-2625.
- [13] T. Advocat, J.L. Crovisier, E. Vernaz, G. Ehret, H. Charpentier, Mater. Res. Soc. Symp. Proc. 212 (1991) 57.
- [14] K. Lemmens, P. Van Iseghem, The effect of gamma radiation on the dissolution of high-level waste glass in Boom Clay, in: K. Hart (Ed.), Scientific Basis for Nuclear Waste Management XXIV, Sydney, Materials Research Society, in press.
- [15] B. Grambow, A general rate equation for nuclear waste glass corrosion, in: Scientific Basis for Nuclear Waste Management VIII, Mater. Res. Soc. Symp. Proc., vol. 44, 1985, p. 15.
- [16] K. Lemmens, The effect of clay on the dissolution of nuclear waste glass, this volume.
- [17] P. Van Iseghem, In situ corrosion tests on HLW glass as part of a larger approach, in: Glass-Scientific Research for High Performance Containment, CEA Valrhô and University of Montpellier, 1997, p. 535.
- [18] S. Gin, P. Jollivet, J.P. Mestre, M. Jullien M., C. Pozo, Appl. Geochem. 16 (7) (2001) 861.