Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH

CORALUS Phase II

Gas Release and Migration in the Boom Clay of Mol

GRS - 216

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Gas Reelase and Migration in the Boom Clay of Mol

Project: “Corrosion of Active Glass in the Underground Conditions“

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1 Introduction

1.1 Objectives

Within the scope of national and international radioactive waste disposal concepts, the intention is to isolate them in deep geological formations in order to avoid the release of radionuclides into the biosphere above an acceptable limit. Besides salt and granite, clay formations are investigated.

For investigating the suitability of clay formations in terms of their physical and chemical behaviour, the Belgian research centre SCK-CEN is performing an in situ test called CORALUS (CORrosion of Active gLass in Underground Storage conditions) in the Boom clay of the Underground Research Facility HADES in Mol /VAL 97/.

The overall objective of the CORALUS project is to study the performance of both active and inactive HLW glass specimens in direct contact with different types of backfill materials under conditions as representative as possible for those expected to prevail in a disposal site in the Boom clay formation (α- and γ-irradiation, temperature, pressure, backfill material, formation water,...). The experimental set-up represents a scenario in which the vitrified waste comes into direct contact with the interacting backfill material and/or the Boom clay.

More specifically, the objectives of the CORALUS project are:

1. **Determination of the glass dissolved under simulated disposal conditions.** Both the integral glass dissolution and the specific release of ^{237}Np, ^{239}Pu and ^{241}Am are measured. The use of coupon glass specimens allows a comparison of these results with those from previous laboratory and in situ tests, as well as an interpretation of the results with the dissolution models based on laboratory tests. Surface and bulk studies of the glasses which have reacted help in elucidating corrosion mechanisms.

2. **Evaluation of the radionuclides migrated through the interacting media in the presence of a radiation field.** Two reference scenarios are studied. The first scenario includes both a γ-radiation field produced by ^{60}Co sources and the α/γ activity in the glass. The temperature at the glass/backfill interface is set to 90 °C in this

scenario. In the second scenario, no external γ-radiation field is created. The temperature at the glass/backfill interface is set at 30 °C. In addition, inactive isotopes, or simulates, of other long-lived nuclides of interest, such as ^{135}Cs, ^{79}Se, ^{93}Zr, ^{107}Pd, are investigated in terms of release and migration in both scenarios 1 and 2.

3. **Measurements and calculations of various parameters in the interacting media** (dose rate, temperature, value of pH and Eh, gas generation and migration, petrophysical properties of the backfill) to determine their effects on the glass dissolution, radionuclide leaching and radionuclide migration. The measurements are compared with the measurements of laboratory tests with the aim of separating the different parameters for gas generation and gas migration.

1.2 Experiment layout

To achieve these objectives, four test tubes, including active and inactive glass samples, different backfill materials, piezometers, heating elements, thermocouples, and (optionally) ^{60}Co sources, were installed in the Boom clay of the URF HADES, which is situated at a depth of 223 m below ground. At different points in time, the interstitial solutions collected in the piezometers are sampled, in order to measure the amount and nature of the dissolved gases and to analyse the ionic composition. After one to four years, the test tubes are retrieved by an overcoring technique. Backfill material is sampled for analysis of the radionuclide migration process, and glass samples are retrieved and analysed. Additional laboratory tests are performed to measure the contribution of gas generation due to backfill heating, and to determine relevant parameters such as porosity, internal surface, and gas diffusivity.

The CORALUS project is performed in collaboration between

- SCK-CEN (Belgium), which designed the instrumentation and installation, performs the test and coordinates the overall project,

- CEA-Valrho (France), which provides the active and inactive glass samples for the test and performs the glass corrosion investigations on the retrieved samples,

- GRS- Braunschweig (Germany), which performs the in situ investigations on gas generation, gas release, permeability of the Boom clay and backfill materials.

Within an additional laboratory programme, the gas generation from the Boom clay and the backfill materials as well as their petrophysical parameters are determined.

The CORALUS project comprises a total of four test tubes, as shown in table 1.1. To demonstrate the feasibility of the assembly, operation, retrieval, dismantling, as well as clay and glass sampling of the active tubes, the inactive tube no. 1 installed in 1998 was loaded with inactive glass samples without a ^{60}Co source. The heating phase extended from 24th February to 21st May, 1999. Afterwards, the tube was dismantled and retrieved. Test tube no. 2 installed in 2000 was loaded with active and inactive glass samples, but not with a ^{60}Co source and heated to 30 °C for about 3.5 years. It simulated a long-term accidental fissure scenario at the disposal site. Test tubes no. 3 and no. 4 were installed in 2002, were loaded with active and inactive glass samples as well as ^{60}Co sources, and were heated to 90 °C for 1.2 and 4.0 years, respectively. These two test tubes do simulate a short-term accidental fissure scenario, occurring after approximately 100 years of cooling time.

Table 1.1 Summary of the four test tubes with their experimental set-up and time frame

Tube No	Glass samples	^{60}Co source	Temperature [°C]	installation	duration of operation
1	inactive	no	90	1998	0.25
2	active+inactive	no	30	2000	3.5
3	active+inactive	yes	90	2002	1.2
4	active+inactive	yes	90	2002	4.0

Each test tube was separated into three independent modules A, B, and C. These modules consist of an inner support tube with flanges and an outer support tube with permeable filter elements. On the inner support tube, eight glass samples (2 inactive and 6 active) were arranged symmetrically. The active samples contain 0.85 per cent (mass content) of $^{237}NpO_2$, $^{238}PuO_2$ or $^{241}Am_2O_3$. The inactive samples contain 0.37 per cent of UO_2 and ThO_2 as well as inactive isotopes of critical long-lived nuclides such as ^{135}Cs, ^{79}Se, ^{93}Zr, ^{107}Pb. The residual volume between the inner and outer support tubes is filled with precompacted semi-cylindrical blocks of dried Boom clay (module A), 60 per cent FoCa clay with 35 per cent sand and 5 per cent graphite (module B), or 95 per cent FoCa clay with 5 per cent inactive glass powder. Two cylindrical piezometers were attached to the inner support tube of each module, and one was attached to the outer support tube. From each of these piezometers, two small tubes ran to a valve panel in the open gallery for gas or water sampling and fluid pressure determination.

The heating elements and thermocouples were mounted on the inner support tube. The ^{60}Co sources were placed in the centre of the inner support tube of each module. The dimensions of a module (diameter x length) were 282 x 263 mm with a ^{60}Co source, and 190 x 263 mm without a ^{60}Co source. The total height of a complete test tube was one metre. The modules of a test tube were mounted on a tube four metres in length to allow positioning farther away from the open gallery, where the clay was less severely disturbed. A three-dimensional cut-away view of a test tube with a ^{60}Co source is shown in figure 1.1.

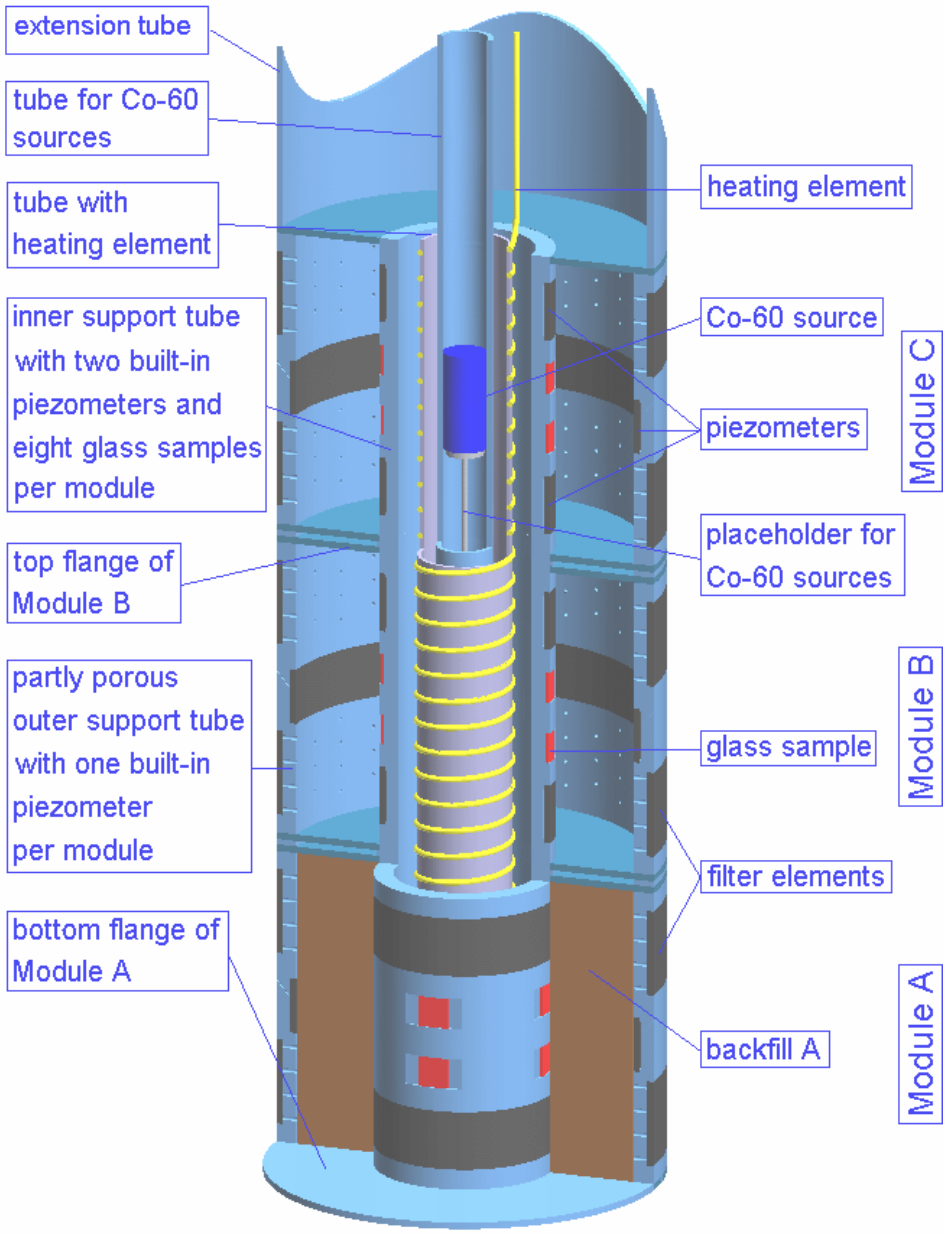

Figure 1.1 Test tube with ^{60}Co source /VAL 97/

The following investigations were performed with all of the test tubes:

- Determination of the interstitial solution by the piezometers
- Determination of the temperature on the inner and outer support tube
- Monitoring of the pH and Eh values of the interstitial solution
- Regular sampling of the interstitial solution from the piezometers for
  - analyses of the dissolved gases
  - analyses of ionic and organic components
- Calculation of the γ-radiation dose rate and temperature profile

2 Programme of investigation at GRS

The investigations at GRS comprise laboratory and in situ measurements on the different backfill materials.

In the course of the laboratory programme, gas generation and gas release from the different backfill materials in contact with air and inert atmosphere in the natural dry and wet stage were determined at temperatures up to 90 °C. In addition, petrophysical parameters such as porosity, gas permeability, and gas diffusivity were measured.

Within the scope of the in situ programme, the gas generation in the different modules, the permeability of the various precompacted and water-saturated backfill materials in the modules, as well as the permeability of the undisturbed Boom clay were determined.

In this report, the results obtained during the period of investigation from September 2000 to March 2005 are presented. It contains the results of the laboratory investigation on gas generation and release from the different backfill materials at a temperature of 90 °C for the exposure periods of 1, 3. 10, 30, 100, 300, and 1000 days as well as the results of the measurements performed at test tube 2, 3, and 4 on the gases dissolved in the interstitial water and the permeability of the backfill materials in test tube 2.

The results of the investigation period 1996 to 2000 are presented in the report GRS-171 /JOC 01/. It contains the results of the laboratory investigation on gas generation and gas release from the different backfill materials at 40 and 90 °C for the exposure period of 100 days as well as the gas diffusivity, gas permeability, internal surface, and pososity of these materials. Furthermore, it contains the results of the measurements performed at test tube no. 1 on the gases dissolved in the interstitial water as well as the permeability of the backfill materials and the surrounding host rock (Boom clay).

3 Methods

3.1 Measurement of gas release from the different backfill materials

Within the scope of the laboratory programme, the gas generation and gas release from the three different backfill materials under defined physico-chemical conditions at 90 °C as a function of time was investigated. Three kilograms of each backfill material were ground, homogenised and then partitioned to samples of 100 grams which were transferred into glass ampoules with a volume of 500 ml as shown in figure 3.1. A three way valve with one outlet connected to a vacuum pump and the other outlet connected to a nitrogen bottle was then attached to the injection tube. The ampoules were evacuated to about 100 Pa and refilled again to atmospheric pressure with nitrogen. Degassed water was then added into the ampoules by a syringe via the rubber hose between the injection tube of the ampoule and the valve. About 12.2 ml water was added to the dried Boom clay (Backfill A), 10.3 ml water was added to the FoCa clay with sand and graphite (Backfill B), and 15.2 ml water was added to the FoCa clay with glass powder (Backfill C). These amounts of water are necessary for reaching a water-saturated stage in the pre-compacted backfill blocks, which were installed in the modules of the test tube. The ampoules were sealed gastight after filling. The exposure periods in the oven at 90 °C were 1, 3, 10, 30, 100, 300, and 1000 days. For statistical reasons three replicates were prepared for each test case that means 21 ampoules for each backfill material. Additionally six ampoules were prepared for blank tests, three with 15 ml of degassed water and nitrogen in the residual volume and three only with nitrogen in the whole volume.

After the envisaged storage at the temperature of 90 °C, the ampoules were withdrawn from the oven for analysis of the generated gases. Each ampoule was connected to a pump stand consisting of a glass transfer tube with connectors, to which two glass bulbs with a defined volume could be attached, as shown in figure 3.2. Each bulb was equipped with a valve and a septum. Gas lines were connected to the end of the transfer tube valve: one for evacuating the whole system and the other for purging it with nitrogen. The entire system was evacuated to a pressure of about 100 Pa by an electric pump, refilled with nitrogen to atmospheric pressure and then evacuated again. This procedure was repeated three times, and at last the system was evacuated.

Afterwards the break seal on the ampoule was opened by dropping a small Teflon®-coated magnet onto it; this allows the gas in the residual volume of the ampoule to enter the void volume of the transfer tube and the two connected bulbs. Nitrogen was then added through the purge line to adjust the pressure throughout the system to 0.15 MPA absolute. The valves of the glass bulbs were closed and then disconnected from the transfer tube. The gas was extracted with a gas syringe through a septum on the bulb and injected into a gas chromatograph (GC) for analysis. The pressure values were recorded after evacuation, after opening the ampoules, and after adding nitrogen.

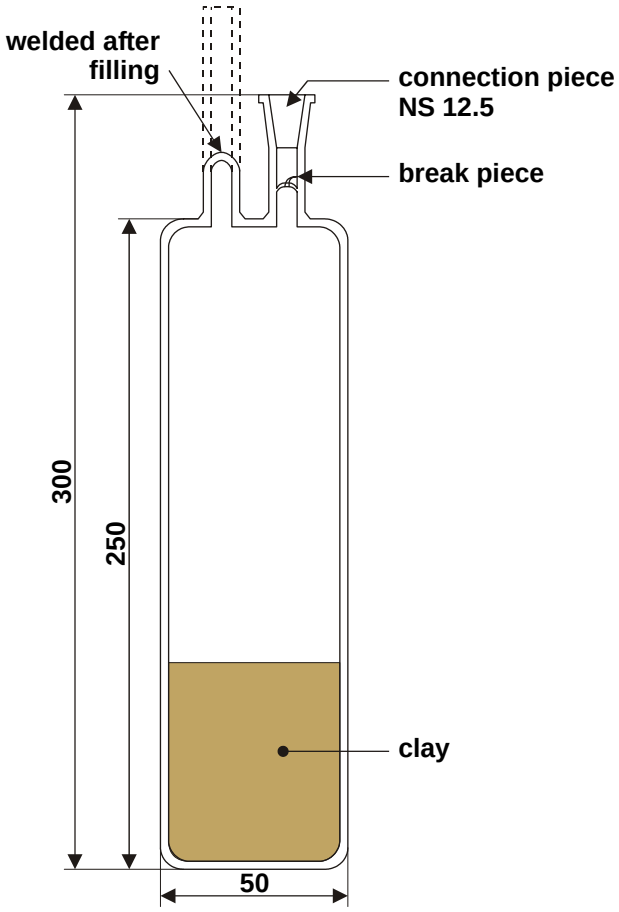

Figure 3.1 Ampoule for the investigation of generation and release of gases from the different backfill materials as a result of elevated temperature

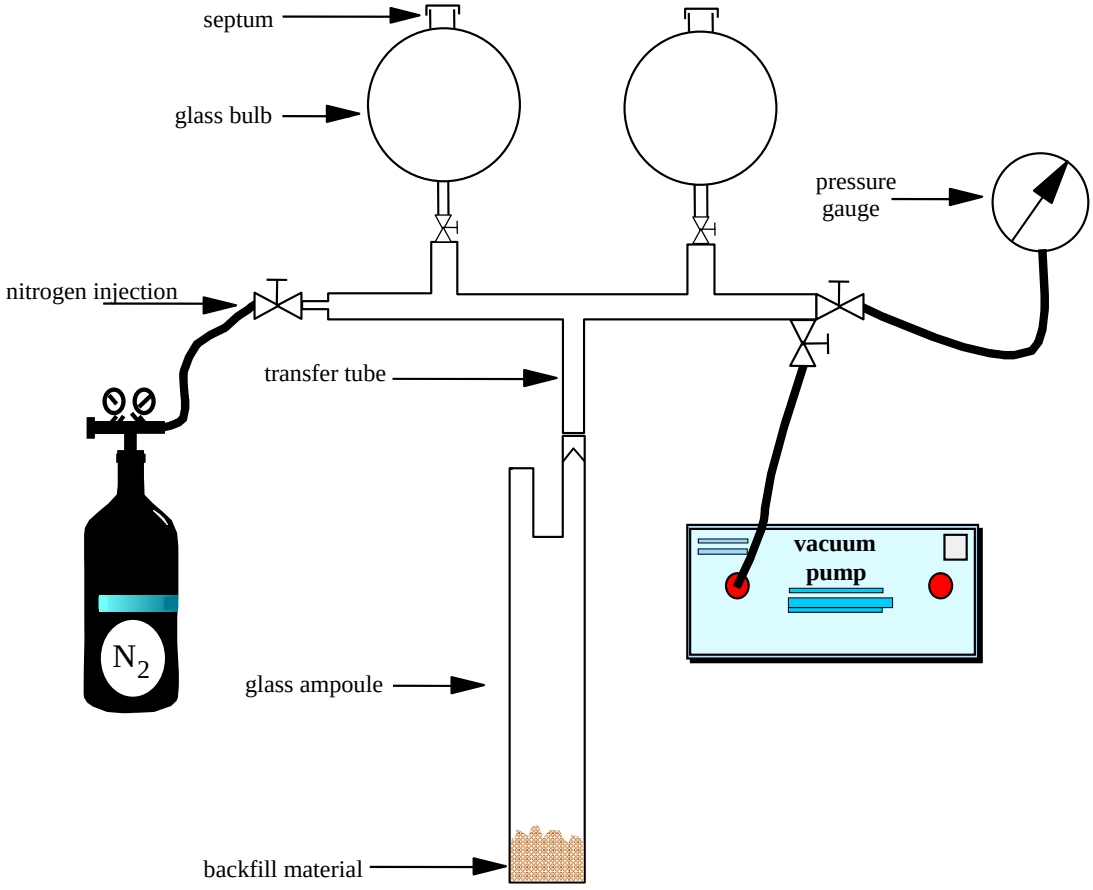

Figure 3.2 Pump stand with transfer tube and glass bulbs for extracting the generate gases from the attached ampoules

3.2 Gases dissolved in the interstitial water

As shown in figure 1.1, the modules A, B, and C with the different backfill materials are equipped with three piezometers each, two on the inner support tube and one on the outer support tube. From each piezometer, two stainless steel tubes run to a valve panel in the open gallery. By means of the piezometers, tubes, and valve panel, the backfill bodies in the modules were flooded with synthetic clay water similar to the formation water of the surrounding Boom clay at the beginning of the test. Gas or water samples were taken from the different piezometers with the use of special stainless steel containers coated with Teflon®. These containers with a volume of 25 or 50 ml were equipped with two valves and quick connectors at both ends. After coupling a sampling container to the valve of a piezometer, it was evacuated to an absolute pres-

sure of about 500 Pa. The valve for evacuating the container was then closed, and the valves to the inlet of the container and the piezometer were opened. Water or gas thus flowed from the piezometer into the container. Nitrogen was injected through the second tube into the piezometer to support the flow of water into the sampling container. The sampling container remained attached until the original pressure in the overall system had again been reached. This ensured that the container was flooded with water or gas from the piezometer. Then all valves were closed, the container was disconnected and sent to GRS in Braunschweig for analysis of the gases. The container was weighed to determine whether a gaseous phase had also been sampled in addition to the liquid phase.

During the time period from beginning of 2001 to end of 2004, water samples from the different piezometers of the test tubes 2, 3, and 4 were analysed in the GRS laboratory in Braunschweig. For performing these analyses, a gas chromatograph system as described in chapter 3.3 was used. The water samples could not be analysed directly. The gases dissolved in the water had to be released and transferred into a matrix gas which then could be injected into the gas chromatograph for determination. For release and transfer three different methods were used in the GRS laboratory in Braunschweig.

1. The water of the 25 or 50 ml sampling container was transferred into an evacuated 500 ml stainless steel degassing container without any contact to the atmosphere. Afterwards the degassing container was flooded with nitrogen to atmospheric pressure. Then this container was sealed gas-tight and stored for 24 hours in an oven at a temperature of 90 °C to release the dissolved gases from the water into the residual volume. By using a syringe, 100 ml of the gas were extracted from the residual volume through a septum attached to the container and injected into a gas chromatograph for qualitative and quantitative analysis. Afterwards the stainless steel container was purged with two litres nitrogen within two minutes. Again it was closed and stored for 24 hours at 90 °C to determine the gases still dissolved as mentioned above. This was repeated three to four times until the gas concentration released into the residual volume was less than 10 % of the concentration after the first heating.

2. Again, the water from the sampling container was transferred into the degassing container which was then sealed. Now the degassing container was stored 24 hour at room temperature (about 22 °C) for determination of the gas release at ambient temperature and afterwards the container was stored at 90

°C for determination of the gas release at elevated temperature. Gas extraction from the container for analyses and rinsing with nitrogen after each step was performed as mentioned above.

3. The water from the sampling container was transferred into the degassing container which was then sealed. Now the degassing container was stored 24 hour at room temperature (about 22 °C) for determination of the gas release at ambient temperature. Instead of heating to 90 °C about 1.0 ml 1 molar HCl was injected into the container to reduce the value of pH of the water to a level below 5. For acceleration of the gas release from the water the container was rotated for one hour. Afterwards 100 ml of the gas in the residual volume were extracted and injected into the gas chromatograph. The residual volume was then purged with nitrogen, the container was sealed again and was rotated for one hour. This was repeated three to four times until the gas concentration released into the residual volume was less than 10 % of the concentration after the first rotation.

Samples taken from April 2001 up to March 2003 were analysed with the 1st method, those taken from June until October 2003 with the 2nd method, and those taken from December 2003 until August 2004 with the 3rd method. The results are presented in section 4.2.

3.3 Gas chromatograph system for analyses

The gas chromatograph system consists of four independent channels, each of which is optimised for detecting a special class of gases. Each channel is equipped with two chromatic columns in series, a guard column and a separation column. The purpose of the guard column is to remove components which may interfere with the detection; the components of interest pass through this column quickly. After all analytes have passed through the guard column, this column is back-flushed by means of a multiposition valve. The analytes are then separated in the separation column. Details of the GC system are listed in table 3.1. The measured signals are recorded, analysed, and archived on a personal computer.

Table 3.1 GC system used for the chromatographic gas analyses

Chromato-graphic channel	A	B	C	D
guard column	Porapak PS acetone-washed 1.0 m 80 - 100 mesh	Porapak T + mol sieve 5 Å 1.0 m + 1.0 m 80 - 100 mesh	Porapak T 1 m 80 – 100 mesh	Porapak QS 0.5 m 80 - 100 mesh
separation column	Porapak PS, acetone-washed 2.0 m 80 - 100 mesh	mol sieve 5 Å 5 m 80 - 100 mesh	mol sieve 5 Å 2.5 m 80 - 100 mesh	Porapak N 2.5 m 80 - 100 mesh
carrier gas	N_2	N_2	He	N_2
detector*	FPD, TCD	TCD	TCD	FID
analysed components	sulphur-containing gases, e.g. H_2S, SO_2	He, N_2O, H_2	Ar, O_2, N_2	**HC: C_1-C_4, CO, CO_2

* FPD: flame photometric detector
TCD: thermal conductivity detector
FID: flame ionisation detector
** HC: hydrocarbons (C1 – C4 with one to four carbon atoms)

3.4 In situ permeability measurements of backfill modules

During the first phase of CORALUS measurements of permeability to gas and to water had been performed in the Boom clay. Gas injection tests had also been conducted in the various backfill modules of the test tube 1, and a first attempt had been made to evaluate the pressure curve obtained during a sampling of interstitial water from the backfill in terms of permeability to water (pressure recovery test) /JOC 01/. Since this appeared promising, it was decided to use a defined procedure of de-pressurizing the different backfill modules of test tube 2 at the end of the experiment in order to obtain reliable data on backfill permeability to water. This procedure was undertaken by SCK-CEN.

On December 16, 2003 the upper central piezometers of each module were first carefully degassed. The piezometer solution was then displaced with nitrogen (2 bar) and replaced by Boom clay pore water, taking care to remove gas bubbles attached on the microtubes. Purging was only stopped when there was no longer gas coming out of the outgoing tube. Then the injected pore water was allowed to expand by the heating to

30 °C (valve on the outgoing tube open) for 30 minutes. Finally, the valve was closed and the pressure recovery recorded.

The recorded pressure curves were evaluated in terms of formation permeability to water with the use of the Weltest 200 computer code /WEL 97/. Details of the evaluation and results are presented in section 4.3.

It had originally been intended to perform similar tests at the CORALUS test tube 3 which had been run at 90 °C. The pressure evolution at this test tube, however, was so disturbed that no evaluation was possible.

4 Results

4.1 Measurements of gas release from the different backfill materials

Within the scope of the laboratory programme, the gas generation and gas release from the three different backfill materials under defined physico-chemical conditions at 90 °C as a function of time as described in section 3.1, was investigated

The results (mean values of the three replicates) are shown in figures 4.1 to 4.3 and in table 4.1. For better comparability, the results are normalised with respect to m^3/1000 kg natural dry material. Blind tests with 15 ml of degassed water and nitrogen or with only nitrogen in the ampoules, handled in the same manner as all the other ampoules, and exposed for 10 and 100 days at 90 °C indicated that all the gases of interest were below the detection limit of the analytical system.

Carbon dioxide is the only gas which was released in significant amounts within 1 000 days at a temperature of 90 °C up to 0.95 m^3/1000 kg from backfill A (dried Boom clay), up to 0.30 m^3/1000 kg from backfill B (60 % FoCa clay with 35 % sand and 5 % graphite) and up to 0.06 m^3/1000 kg from backfill C (95 % FoCa clay with 5 % glass powder). The amount is still increasing with time, especially in backfill A and backfill B. It is most likely that carbon dioxide is generated by oxidation of organic materials or the graphite in the presence of oxygen adsorbed to the clay. The FoCa clay has a low content of organic material which results in lower generation of carbon dioxide from the backfill B and C. The graphite in backfill B may also be oxidised even at 90 °C as the release of carbon dioxide is by a factor of 6 higher than from backfill C with a higher content of FoCa clay, but no graphite. Additionally, it is most likely that carbon dioxide is generated by oxidation of organic materials in the presence of oxygen adsorbed on the clay, or by thermal decomposition of carbonates within the clay. Boom clay and FoCa clay contain about 1 % of calcite ($CaCO_2$) (mass content), which could be decomposed thermally in the presence of the synthetic formation water.

Hydrogen is generated up to 0.08 m^3/1000 kg from backfill A and up to 0.006 m^3/1000 kg from backfill B and C within 1 to 3 days of heating. Later on, its amount decreases, obviously by oxidation and back reaction. Below the combustible concentration of oxygen and hydrogen calm reactions take place generating hydrogen

peroxide and hydrogen oxygen radicals which itself decomposes at elevated temperature /ATK 01/ and /MOO 76/.

Methane was only detected in the ampoules with backfill B and in the ampoules with backfill C when heating longer than 100 days. The released amount is up to 0.0008 m^3/1000 kg. Further hydro carbons and further gases were below the detection limit of the gas chromatograph and therefore do not seem to be of importance.

For long term safety aspects the amount of the generated and released hydrogen and of the hydrocarbons are not of importance for they will be dissolved in the pore and interstitial water of the clay. The Boom clay and the buffer materials contain at least 100 to 150 litre of water per 1000 kg. The Bunsen coefficient (solubility of the gas in water at 20 °C and 1 bar) are for methane 0.035 litres per kg water and for hydrogen 0.0178 litres per kg water. These figures indicate that with a water content of 100 litres per 1000 kg clay up to 3.5 litres of methane and up to 1.78 litres hydrogen could be dissolved which is much more than the generated amount of the gases per 1000 days.

The Bunsen coefficient for carbon dioxide is 0.87 litres per kg water which indicates that up to 87 litres could be dissolved within 1000 kg clay with a water content of 100 litres. This is much less than the amount of carbon dioxide generated within 1000 days in backfill A (950 litres per 1000 kg) and in Backfill B (300 litres per 1000 kg). For the long term safety aspects it has to be taken into account that the gas generation is a slow process and that the diffusivity for carbon dioxide in the water saturated backfill material determined during the CORALUS 1 project /JOC 01/ is higher than $0.1 \cdot 10^{-9}$ m^2/s. During generation carbon dioxide will migrate into the surrounding host rock where it could be stored without any problem. Nevertheless it should be worthwhile to perform modelling on carbon dioxide generation, carbon dioxide migration into the surrounding host rock and pressure build up at the conditions of a repository.

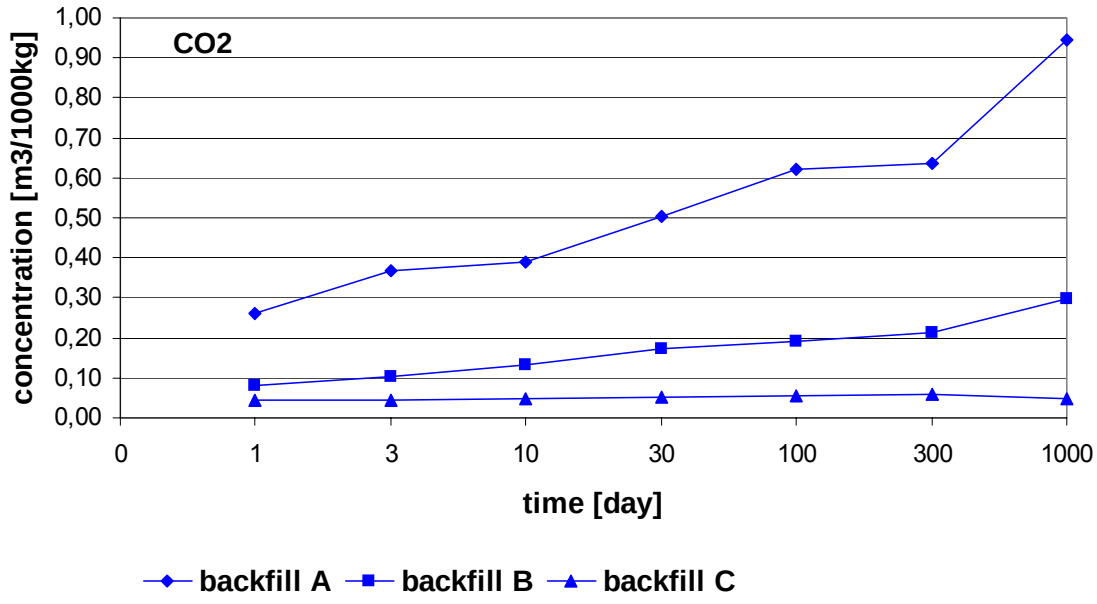

Figure 4.1 Release of carbon dioxide from the different backfill materials in the natural dry stage with nitrogen in the residual volume of the ampoules at 90 °C as a function of time. Boom clay (A), FoCa clay with sand and graphite (B), FoCa clay with glass powder (C)

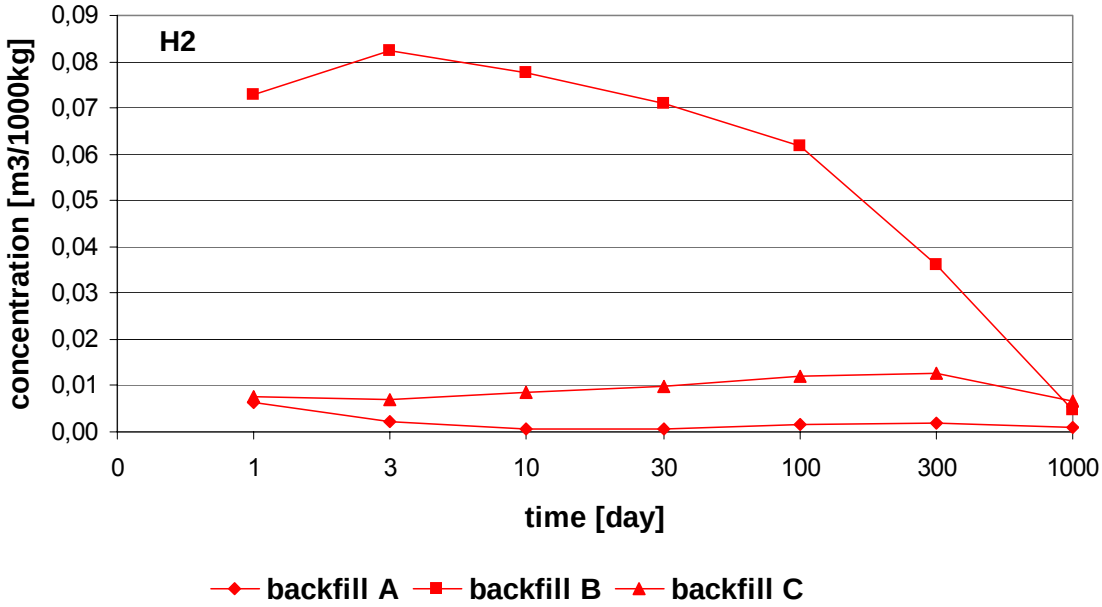

Figure 4.2 Release of hydrogen from the different backfill materials in the natural dry stage with nitrogen in the residual volume of the ampoules at 90 °C as a function of time. Boom clay (A), FoCa clay with sand and graphite (B), FoCa clay with glass powder (C)

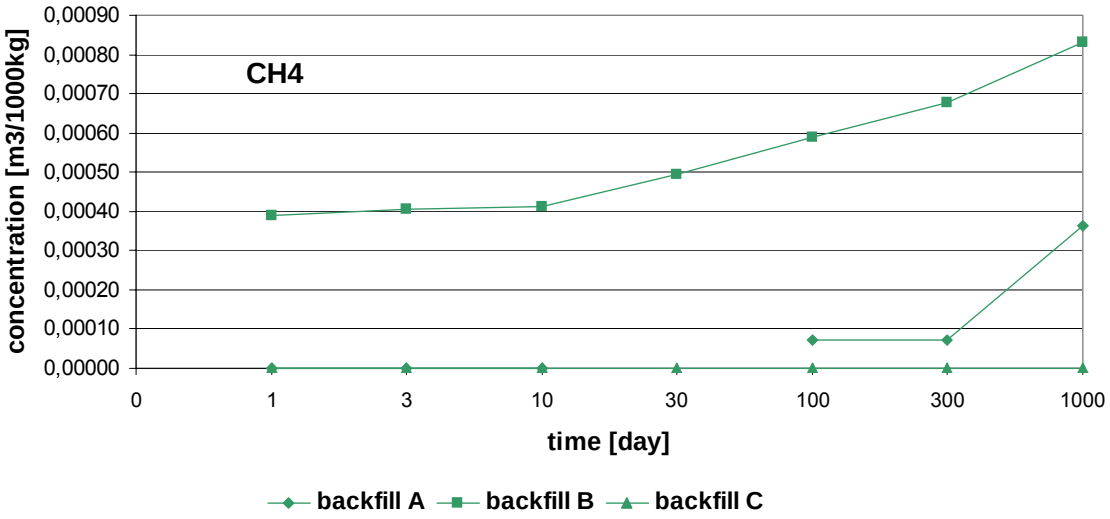

Figure 4.3 Release of methane from the different backfill materials in the natural dry stage with nitrogen in the residual volume of the ampoules at 90 °C as a function of time. Boom clay (A), FoCa clay with sand and graphite (B), FoCa clay with glass powder (C)

Table 4.1 Mean values of the gas components carbon dioxide, hydrogen, and methane released from the different natural dry backfill materials into the residual volumes of the ampoules flooded with nitrogen; exposure temperature 90 °C

A: dried Boom clay

B: 60 % FoCa clay with 35 % sand and 5 % graphite

C: 95 % FoCa clay with 5 % glass powder

amount of water added [ml/100 grams]	exposure time [days]	specific amount of released gases [m³/1000kg]		
		backfill A	backfill B	backfill C
		carbon dioxide		
12,2	1	0,2615	0,0793	0,0443
12,2	3	0,3693	0,1012	0,0432
12,2	10	0,3906	0,1339	0,0469
12,2	30	0,5052	0,1715	0,0516
12,2	100	0,6220	0,1906	0,0548
12,2	300	0,6370	0,2142	0,0575
12,2	1000	0,9483	0,2968	0,0463
		hydrogen		
10,3	1	0,0063	0,0728	0,0076
10,3	3	0,0021	0,0823	0,0071
10,3	10	0,0007	0,0778	0,0084
10,3	30	0,0006	0,0711	0,0098
10,3	100	0,0016	0,0618	0,0121
10,3	300	0,0018	0,0361	0,0127
10,3	1000	0.0009	0,0046	0,0064
		methane		
15,2	1	n.m.	0,00039	n.m.
15,2	3	n.m.	0,00041	n.m.
15,2	10	n.m.	0,00041	n.m.
15,2	30	n.m.	0,00049	n.m.
15,2	100	0,00007	0,00059	n.m.
15,2	300	0,00007	0,00068	n.m.
15,2	1000	0,00038	0,00083	n.m.

n.m. = not measurable

4.2 Gases dissolved in the interstitial water

The gases dissolved in the interstitial water which was extracted from the piezometers installed in the different backfill materials at the test tubes 2, 3, and 4 are listed up in table 4.2.

The most important components are carbon dioxide, hydrogen, methanes and oxygen. Additionally, small amounts of hydrogen sulphide were determined, almost below the detection limit (0.2 litre gas per m^3 water) and only once up to 8.6 litre gas per m^3 water (tube 4 A1 26.06.2003). The diagrams of the gas chomatograph showed further sulphur components below the detection limit. Generally, the water and the gases extracted from the different piezometers had a smell similar to hydrogen sulphide or mercaptans.

The results of the gas content in the water extracted from the different piezometers show high variations. These variations are caused by:

1. Insufficient gas tightness of the test system. The gases generated in the backfill materials can migrate (advection and diffusion) into the open gallery when the gas pressure or the gas concentration increases.

2. Diffusion of the gases from the area close to the heater into the surrounding host rock. In the CORALUS I project /JOC 01/ the diffusivities for the different gases were determined. In the water saturated stage of the backfill material the diffusivity for carbon dioxide is in the range of 10^{-9} m²/s and those of hydrogen and methane in the range of 10^{-11} m²/s. If the material is not fully saturated, the values are by a factor of 10 to 100 higher.

3. Dilution as a result of water extraction from the piezometers and renewing the extracted amount.

Nevertheless, the results indicate that the concentrations of the gas components hydrogen and carbon dioxide in the interstitial water from the test tubes 3 and 4 with a temperature of 90 °C and ^{60}Co-soures are significantly higher than in the interstitial water from test tube 2 with a temperature of 30 °C and without ^{60}Co-sources. At test tube 2 the concentration of methane is significantly higher than at test tubes 3 and 4. This fact indicates that methane is decomposed by γ-irradiation generating hydrogen

and higher hydro carbons /LIE 91/. Furthermore at the temperature of 30 °C without irradiation microbial activities may influence the whole gas generation and release.

The values of oxygen may be influenced by the untightness of the system and by contamination with air during sampling in the test field or handling of the samples in the laboratory. Therefore they are sometimes unrepresentatively high. The concentration of oxygen above 400 litres per 1000 kg should be skipped.

Table 4.2 Dissolved gases in the water samples from the piezometers of tube 2, 3, and 4, of the CORALUS II project

Tube 2: 30 °C without Co60 sources, operation period March 2001 to December 2003

date of sampling	water from	degassing temperature and condi-tion	released amount of the gas components [l/1000kg]				
			H_2	H_2S	CO_2	CH_4	O_2 + Ar
12.04.2001	A3	90 °C	n.t.	n.t.	108,40	n.t.	42,48
12.04.2001	B3	90 °C	n.t.	n.t.	28,14	n.t.	30,32
12.04.2001	C3	90 °C	n.t.	n.t.	36,18	n.t.	15,22
10.05.2001	A1	90 °C	n.t.	n.t.	156,47	n.t.	60,22
10.05.2001	B1	90 °C	n.t.	n.t.	60,28	n.t.	70,93
10.05.2001	C1	90 °C	n.t.	n.t.	46,34	n.t.	69,91
29.11.2001	A2	90 °C	n.t.	n.t.	141,11	105,47	29,58
29.11.2001	B2	90 °C	n.t.	n.t.	108,03	76,18	27,50
29.11.2001	C2	90 °C	n.t.	n.t.	72,80	0,27	43,29
29.11.2001	synth. solut.A	90 °C	n.t.	n.t.	171,61	n.t.	20,20
29.11.2001	synth. solut.B	90 °C	0,12	n.t.	11,63	n.t.	681,35
29.11.2001	synth. solut.C	90 °C	0,18	n.t.	147,02	n.t.	14,63
07.05.2002	A3	90 °C	n.t.	n.t.	202,36	2,85	2407,93
07.05.2002	B3	90 °C	n.t.	n.t.	39,43	0,28	1589,33
07.05.2002	C3	90 °C	n.t.	n.t.	136,27	n.t.	1325,50
17.09.2002	A1	90 °C	n.t.	n.t.	177,24	1,46	218,05
17.09.2002	B1	90 °C	n.t.	n.t.	26,36	0,63	274,03
17.09.2002	C1	90 °C	n.t.	n.t.	113,64	n.t.	450,81
23.01.2003	A3	90 °C	n.t.	n.t.	82,77	26,64	81,68
23.01.2003	B3	90 °C	n.t.	n.t.	29,50	34,37	151,58
23.01.2003	C3	90 °C	n.t.	n.t.	98,18	0,76	124,02
continuation Tube 2: 30 °C without Co60 sources,							

Table 4.2 Continuation

Tube 2: 30 °C without Co60 sources, operation period March 2001 to December 2003

date of sampling	water from	degassing temperature and condi-tion	released amount of the gas components [l/1000kg]				
			H_2	H_2S	CO_2	CH_4	O_2
24.09.2003	A1	25 °C	n. t.	n.t.	48,66	1,02	784,83
		90 °C	n.t.	n.t.	77,46	n.t.	7,73
24.09.2003	B1	25 °C	n.t.	n.t.	7,99	n.t.	76,15
		90 °C	n.t.	n.t.	15,32	n.t.	14,72
24.09.2003	C1	25 °C				.	.
	leakage	90 °C				.	.
30.01.2004	A3	25 °C	n.t.	n.t.	20,62	21,89	42,98
		25 °C + HCl	n.t.	n.t.	618,21	13,03	n.t.
30.012004	B3	25 °C	0,09	n.t.	2,31	44,62	24,14
		25 °C + HCl	n.t.	n.t.	139,40	26,17	n.t.
30.01.2004	C3	25 °C	0,38	n.t.	10,60	3,62	12,49
		25 °C + HCl	n.t.	n.t.	154,55	3,51	n.t.
16.06.2004	A1	25 °C	0,55	n.t.	9,82	13,70	11715,25
		25 °C + HCl	n.t.	n.t.	122,81	68,43	n.t.
16.06.2004	B1	25 °C	n.t.	n.t.	19,12	12,66	50,15
		25 °C + HCl	n.t.	n.t.	64,90	10,28	n.t.
16.06.2004	C1	25 °C	n.t.	n.t.	9,44	0,25	42,56
		25 °C + HCl	n.t.	n.t.	45,80	n.t.	51,59
16.06.2004	A2	25 °C	0,14	n.t.	5,06	7,04	11,20
		25 °C + HCl	n.t.	n.t.	366,91	n.t.	n.t.
06.16.2004	B2	25 °C	0,02	n. t.	0,85	0,47	40,10
		25 °C + HCl	n.t.	n.t.	305,70	0,61	n.t.
16.06.2004	C2	25 °C	n.t.	n.t.	1,04	n.t.	40,49
		25 °C + HCl	n.t.	n.t.	337,91	n.t.	61,63

Table 4.2 Continuation

Tube 3: 90 °C with Co60 sources, operation period January 2003 to March 2004

date of sampling	water from	degassing temperature and condi-tion	released amount of the gas components [l/1000kg]				
			H_2	H_2S	CO_2	CH_4	O_2 + Ar
05.03.2003	A3	90 °C	n.t.	n.t.	509,09	1,35	111,15
05.03.2003	B3	90 °C	26,58	n.t.	193,60	1,13	327,32
05.03.2003	C3	90 °C	analyses	were not	possible	not enough	water
06.08.2003	A1	25 °C	0,85	n.t.	273,91	1,44	341,72
		90 °C	n.t.	n.t.	399,82	1,26	414,53
06.08.2003	C1	25 °C	n.t.	n.t.	128,73	n.t.	48,58
		90 °C	n.t.	n.t.	189,37	n.t.	29,55
01.12.2003	A2	25 °C	n.t.	n.t.	46.68	n.t.	n.t.
	leakage	25 °C + HCl					
01.12.2003	B2	25 °C	n.t.	n.t.	99,48	n.t.	977,76
		25 °C + HCl	n.t.	n.t.	500,78	n.t.	144,54
01.12.2003	C2	25 °C	2,79	n.t.	69,34	n.t.	38,64
		25 °C + HCl	n.t.	n.t.	397,38	n.t.	32,20
22.01.2004	A3	25 °C	n.t.	n.t.	n.t.	n.t.	n.t.
		25 °C + HCl	n.a.t.	n.t.	1029,32	2,71	238,18.
22.01.2004	B3	25 °C	n.t.	n.t.	n.t.	n.t.	n.t.
	leakage	25 °C + HCl					n.t.
22.01.2004	C3	25 °C	n.t.	n.t.	n.t.	n.t.	n.t.
	leakage	25 °C + HCl					
01.04.2004	C1	25 °C	3,09	n.t.	11,32	0,24	22,43
		25 °C + HCl	4,24	n.t.	139,76	n.t.	n.t.
01.04.2004	C2	25 °C	0,1	n.t.	7,37	0.07	n.t.
		25 °C + HCl	n.t.	n.t.	121,41	n.t.	n.t.

Table 4.2 Continuation

Tube 4: 90 °C with Co60 sources, operation period January 2004 to June 2007

date of sampling	water from	degassing temperature and condi-tion	released amount of the gas components [l/1000kg]				
			H_2	H_2S	CO_2	CH_4	O_2
26.06.2003	A1	25 °C	n.t.	5,13.	123,63	2,42	256.36
		90 °C	n.t.	3,47	365,94	2,20	229,30
26.06.2003	B1	25 °C					
	leakage	90 °C					
26.06.2003	C1	25 °C	2,36	n.t.	43,22	1,06	166,98
		90 °C	n.t.	n.t.	103,38	0,91	144,50
24.10.2003	A3	25 °C	2,15	n.t.	128,11	3,39	209,62
		90 °C	n.t.	n.t.	182,75	n.t.	80,13
24.10.2003	A3	25 °C	n.t.	n.t.	131,32	4,45	44,50
	leakage	90 °C					
24.10.2003	A3	25 °C	0,95	n.t.	353,23	9,51	76,08
		90 °C	n.t.	n.t.	197,16	n.t.	n.t.
31.08.2004	A3	25 °C	n.t.	n.t.	67,98	23,50	1561,88
		25 °C + HCl	analyses	were not	possible.	not enough.	water.
31.08.2004	B3	25 °C	11,38	n.t.	38,64	1,10	57,23
		25 °C + HCl	10,23	n.t.	302,24	1,00	n.t.
31.08.2004	C3	25 °C	4,35	n.t.	20,94	0,46	50,24
		25 °C + HCl	5,72	n.t.	104,05	n.t.	14,28

n. t. = less than the detection limit of about 0,3 l/1000kg
n. a. = not analysed

4.3 Permeability of the backfill materials to water

The pressure evolution during the pressure recovery tests performed in the three backfill modules (A: Boom clay, B: FoCa clay + sand + graphite, C: FoCa clay + glass) of CORALUS tube 2 in December 2003 is shown in Figure 4.1. While the pressure build-up is in principle similar in the various curves, there is some difference in the early-time behaviour. A nearly ideal curve is the one measured in backfill B, starting with a high pressure increase rate which is steadily getting slower. The other two curves start with a lower slope, accelerating and the decelerating again. This is probably due to the piezometers not completely filled with liquid, with a small amount of gas damping the pressure increase. This had already been observed during the first tests in the frame of the CORALUS 1 phase. It can therefore be expected that the pressure curve of backfill B would yield the most reliable results on permeability.

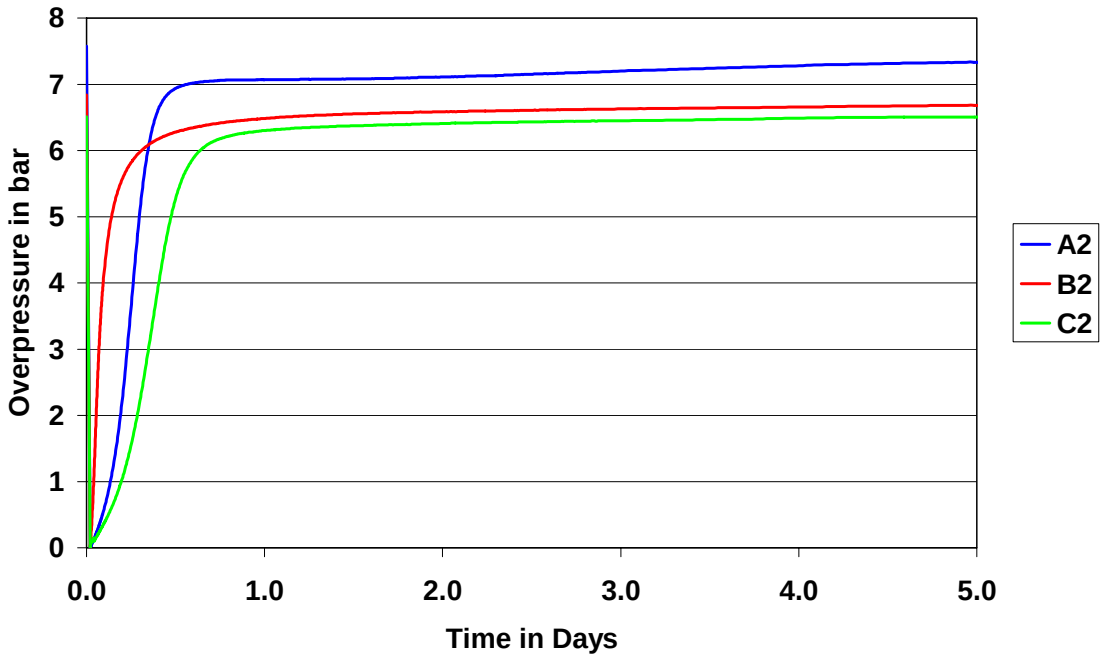

Figure 4.4 Pressure recovery in the piezometers A2, B2, and C2 located in the different backfill modules of test tube 2 after depressurizing on December 16, 2003

For the evaluation of the pressure curves in terms of permeability with the Weltest 200 code /WEL 97/, the following assumptions were made:

- The backfill body is homogeneous, and flow is strictly radial.
- The initial pore water pressure corresponds to the actually measured values.
- The porosity is 40%.

In Figure 4.2, the pressure data measured for the piezometer 2 in backfill B are shown together with the calculated curve for a permeability of $2 \cdot 10^{-18}$ m^2 which exhibits a nearly perfect agreement.

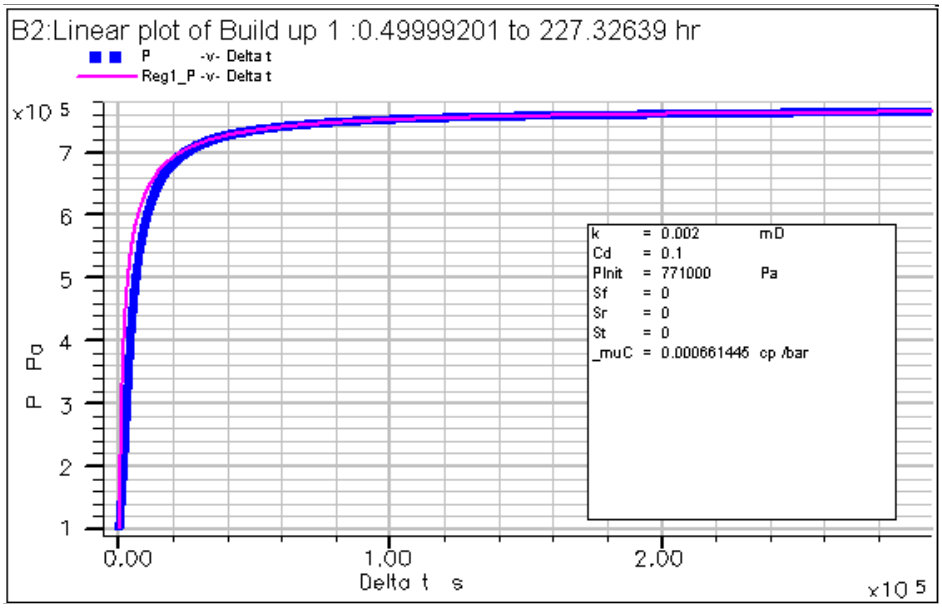

Figure 4.5 Measured (blue) and calculated (pink) pressure recovery in piezometer B2 located in the FoCa clay/sand backfill B after depressurizing on December 16, 2003

The evaluation of the pressure data of the piezometers A2 and C2 yielded less satisfying fits (Figure 4.3 and 4.4, respectively), still, the best results were obtained with a permeability identical to B2, meaning that a permeability of about of $2 \cdot 10^{-18}$ m^2 can be considered rather well established for all three backfill modules. This value is somewhat higher than the permeability of $6 \cdot 10^{-19}$ m^2 which was obtained during the first tests performed in the frame of the CORALUS 1 /JOC 01/, however, the test tube 1 had been run at a temperature of 90 °C instead of 30 °C of the CORALUS 2, which is probably the reason for this difference.

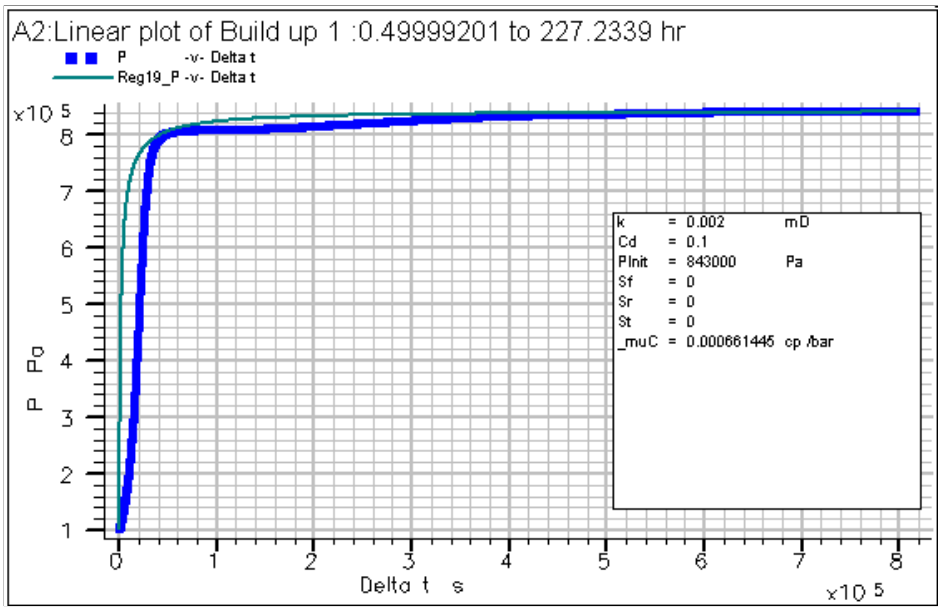

Figure 4.6 Measured (blue) and calculated (green) pressure recovery in piezometer A2 located in the Boom clay backfill A after depressurizing on December 16, 2003

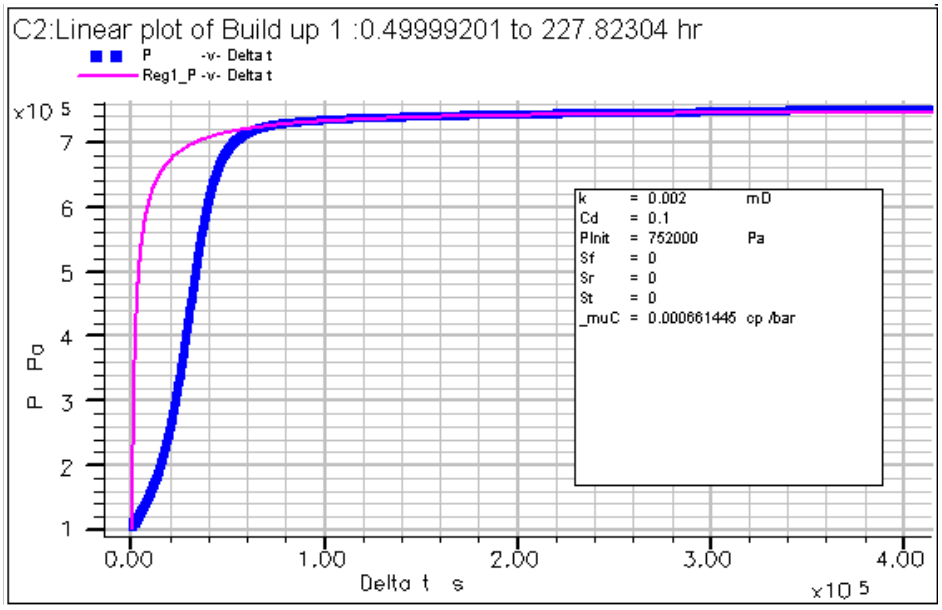

Figure 4.7 Measured (blue) and calculated (pink) pressure recovery in piezometer C2 located in the FoCa clay/glass powder backfill C after depressurizing on December 16, 2003

5 Summary and Conclusions

Within the scope of national and international radioactive waste disposal concepts, the intention is to isolate them in deep geological formations in order to avoid the release of radionuclides into the biosphere above an acceptable limit. Besides salt and granite, clay formations are investigated.

At the underground Research facility HADES in Mol (Belgium) SCK-CEN performs the in situ test called CORALUS for determining the physico-chemical behaviour of the Boom clay with regard to disposing high-level radioactive waste.
The objectives of the CORALUS project are:

- Determination of the glass dissolved under simulated disposal conditions.
- Evaluation of the radionuclides migrated through the interacting media in the presence of a radiation field
- Measurements and calculations of various parameters in the interacting media (dose rate, temperature, value of pH and Eh, gas generation and migration, petrophysical properties of the backfill)

In situ measurements were performed on the inactive test tube 1 in 1999 to prove the feasibility of the three future tests (tube 2, 3, and 4) with ^{60}Co sources and active glass samples. The aim of these active tests, which were performed from 2000 to 2004, was to obtain data for long-term safety calculations on the following subjects:

- dissolution of the glass under simulated disposal conditions;
- migration of the radionuclides through the interacting media, in the presence of a radiation field;
- parameters in the interacting media (dose rate, temperature, pH value, Eh value, gas generation and migration, and petrophysical properties of the backfill).

The CORALUS project is performed in collaboration between

- SCK-CEN (Belgium), which designed the instrumentation and installation, performs the test and coordinates the overall project,

- CEA-Valrho (France), which provides the active and inactive glass samples for the test and performs the glass corrosion investigations on the retrieved samples,

- GRS- Braunschweig (Germany), which performs the in situ investigations on gas generation, gas release, permeability of the Boom clay and backfill materials.

The CORALUS project comprises a total of four test tubes. To demonstrate the feasibility of the assembly, operation, retrieval, dismantling, as well as clay and glass sampling of the active tubes, the inactive tube no. 1 installed in 1998. Test tube no. 2 installed in 2000 was loaded with active and inactive glass samples, but not with a ^{60}Co source and heated to 30 °C for about 3.5 years. Test tubes no. 3 and no. 4 were installed in 2002, were loaded with active and inactive glass samples as well as ^{60}Co sources, and were heated to 90 °C for 1.2 and 4.0 years, respectively. These different test tubes simulated the different stage of the long term safety aspect.

In this report, the results obtained during the period of investigation from September 2000 to March 2005 are presented. It contains the results of the laboratory investigation on gas generation and release from the different backfill materials at a temperature of 90 °C for the exposure periods of 1, 3. 10, 30, 100, 300, and 1000 days as well as the results of the measurements performed at test tube 2, 3, and 4 on the gases dissolved in the interstitial water and the permeability of the backfill materials.

Within the scope of the laboratory programme, the gas release from the backfill materials was determined as a function of time (1 to 1000 days) at temperatures 90 °C, in contact nitrogen (inert atmosphere), and with additional water to simulate the saturated stage.

Carbon dioxide is the only gas which was released in significant amounts within 1 000 days at a temperature of 90 °C up to 0.95 m^3/1000 kg from backfill A (dried Boom clay), up to 0.30 m^3/1000 kg from backfill B (60 % FoCa clay with 35 % sand and 5 % graphite) and up to 0.06 m^3/1000 kg from backfill C (95 % FoCa clay with 5 % glass powder). The amount is still increasing with time, especially in backfill A and backfill B. It is most likely that carbon dioxide is generated by oxidation of organic materials or the graphite in the presence of oxygen adsorbed to the clay. The FoCa clay has a low content of organic material which results in lower generation of carbon dioxide from the backfill B and C. The graphite in backfill B may also be oxidised even at 90 °C as the release of carbon dioxide is by a factor of 6 higher than from backfill C with a higher content on FoCa clay but no content of graphite. Additionally, it is most likely that carbon dioxide is generated by thermal decomposition of carbonates within the clay. Boom clay and FoCa clay contain about 1 per cent of calcite ($CaCO_2$) (mass content), which could be

decomposed thermally in the presence of the synthetic formation water. It seems that in clay formations all the organic material will be transformed to carbon dioxide at elevated temperature at the presence of oxygen. In order to minimise the generation of carbon dioxide, oxygen has to be minimised in the sealed areas of a repository. The amount of carbon dioxide could not be dissolved in the formation water of the surrounding host rock therefore it may be of importance for disposing heat generating high level radioactive waste in clay formations. The generated and released carbon dioxide will pressurize the residual volumes in the disposal areas and it will create fractures if the pressure is above the main stress of the host rock. It should be worthwhile to perform further investigation and modelling on the behaviour carbon dioxide under the physico-chemical conditions of a repository.

Hydrogen is generated up to 0.08 m^3/1000 kg from backfill A and up to 0.006 m^3/1000 kg from backfill B and C within 1 to 3 days of heating. Later on, its amount decreases, obviously by oxidation and back reaction. The amount of hydrogen seems not to be of importance, for the concentration in the pore volume in the presence of oxygen will be far below an ignitable composition. Furthermore, the contribution to the pressure increase compared to the amount of carbon dioxide is almost by the factor of 10 less. The amount of hydrogen could be dissolved in the formation water of the surrounding host rock.

Methane was only detected in the ampoules with backfill B and in the ampoules with backfill C when heating longer than 100 days. The released amount is up to 0.0008 m^3/1000 kg. Further hydro-carbons and further gases were below the detection limit of the gas chromatograph and therefore they do not seem to be of importance. The amount of methane also seems not to be of importance, for concentration in the pore volume in the presence of oxygen will be far below an ignitable composition and the contribution to the pressure increase compared to the amount of carbon dioxide is almost by the factor of 1000 less. The amount of methane could be dissolved in the formation water of the surrounding host rock.

For determining the gas generation and the gas release at the test tube 2, 3, and 4 water samples were take from the piezometers installed at the inner and outer support tubes in the modules with the different backfill materials. The dissolved gases in these water samples were analysed at GRS-Braunschweig.

The most important components are carbon dioxide, hydrogen, methane and oxygen. Additionally, small amounts of hydrogen sulphide were determined, almost below the detection limit. The water and the released gases had a smell similar to hydrogen sulphide or mercaptans.

The gases dissolved in the interstitial water are generated by oxidation of the organic matters (CO_2), by corrosion of metals in the test field (H_2), and by thermal, radiolytical, or microbial decomposition of the water or organic matter in the different clays (CO_2, hydro-carbons).

The results indicate that the concentrations of the gas components hydrogen and carbon dioxide in the interstitial water from the test tubes 3 and 4 with a temperature of 90 °C and ^{60}Co-soures are significantly higher than in the interstitial water from test tube 2 with a temperature of 30 °C and without ^{60}Co-sources. This means these gases are generated by radiolytical or thermal decomposition of water or organic matter in the backfill material. At test tube 2 the concentration of methane is significantly higher than at test tubes 3 and 4. This fact indicates that methane is oxidising at 90 °C and γ-irradiation generating carbon dioxide and consuming oxygen. Therefore, the concentration of oxygen decreases slightly with time. The values of oxygen may be influenced by the untightness of the system and by contamination with air during sampling in the test field or handling of the samples in the laboratory. Therefore, they are sometimes unrepresentatively high.

The laboratory investigation on gas generation indicated significantly different amounts of gases released from the different backfill materials. With regard to carbon dioxide, the released amounts within 300 days at 90 °C are:

backfill A about 0.63 m³/1000 kg
backfill B about 0.22 m³/1000 kg
backfill C about 0.07 m³/1000 kg.

The amounts of carbon dioxide analysed in the interstitial water from the piezometers in the various backfill materials do not show similar differences. Also, there are no differences concerning the piezometers 1 or 2 installed close to the heater tube and piezometer 3 installed at the inner support tube about 10 cm apart from the heater. There is almost a homogeneous distribution of the gases dissolved in the interstitial water. These facts indicate that the generated gases are diffusing from the heater into the surrounding host rock.

The permeability to water of the different backfill materials was determined to be about $2 \cdot 10^{-18}$ m^2. The value is somewhat higher than the $6 \cdot 10^{-19}$ m^2 obtained during earlier measurements, however, these had been performed under different conditions (at a temperature of 90 °C instead of 30 °C).

On the whole, the laboratory and in situ investigations in the CORALUS project have indicated that the gases generated and released during the disposal of radioactive waters in clay formation similar to the Boom Clay will not pressurise sealed areas. They are migrating by advective and diffusive flow into the surrounding host rock. Nevertheless the components carbon dioxide and hydrogen sulphide may be of importance as they alter the values of pH and Eh and may enhance the corrosion of the waste container, the metallic waste, or the solidification matrix.

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