Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH

Gas Release and Migration in the Boom Clay of Mol within the Project „Corrosion of Active Glass in the Underground Conditions" (CORALUS)

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Norbert Jockwer
Klaus Wieczorek

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1   Introduction

Within the scope of national and international radioactive waste disposal concepts, the intention is to dispose of radioactive waste in deep geological formations, in order to isolate them from the biosphere and avoid the release of radionuclides 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, because of the occurrence of fissures in the waste canisters and the metallic overpack.

More specifically, the objectives of the CORALUS project are:

1. to determine the dissolution of the glass 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. to evaluate the migration of the radionuclides 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 40 °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. to measure or to calculate various parameters in the interacting media (dose rate, temperature, pH-value, Eh, gas generation and migration, as well as petrophysical properties of the backfill), and to determine their effects on the glass dissolution and the radionuclide leaching and 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.

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, are placed in the Boom clay. By a four metre long stainless steel tube, they are connected to the URF HADES, which is situated at a depth of 223 m in the Boom clay formation. 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 with

- 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 and release, permeability of the Boom clay and backfill materials, and an additional laboratory programme on gas generation from the Boom clay and backfill materials, as well as their petrophysical parameters.

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 was loaded with inactive glass samples without a ^{60}Co source and installed in 1998. The heating phase extended from 24th February to 21st May, 1999. Afterwards, the tube was dismantled and retrieved. Test tube no. 2 was installed in 1999. It was loaded with active and inactive glass samples, but not with a ^{60}Co source, and will be heated to 40 °C for about 2.5 years. It will simulate a long-term accidental fissure scenario at the disposal site. Test tubes no. 3 and no. 4 will be installed in 2000, will be loaded with active and inactive glass samples as well as ^{60}Co sources, and will be heated to 90 °C for 2.0 and 4.0 years, respectively. These two test tubes will 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	40	1999	2.5
3	active+inactive	yes	90	2000	2.0
4	active+inactive	yes	90	2000	4.0

Each test tube is 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) are 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 are attached to the inner support tube of each module, and one is attached to the outer support tube. From each of these piezometers, two small tubes are routed to a valve panel in the open gallery for gas or water sampling and fluid pressure determination. The heating elements and thermocouples are mounted on the inner support tube. The ^{60}Co sources are placed in the centre of the inner support tube of each module. The dimen-

sions of a module (diameter x length) are 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 is one metre. The modules of a test tube are mounted on a tube four metres in length to allow positioning farther away from the open gallery, where the clay is less severely disturbed. A three-dimensional cut-away view of a test tube with a ^{60}Co source is shown in figure 1.1.
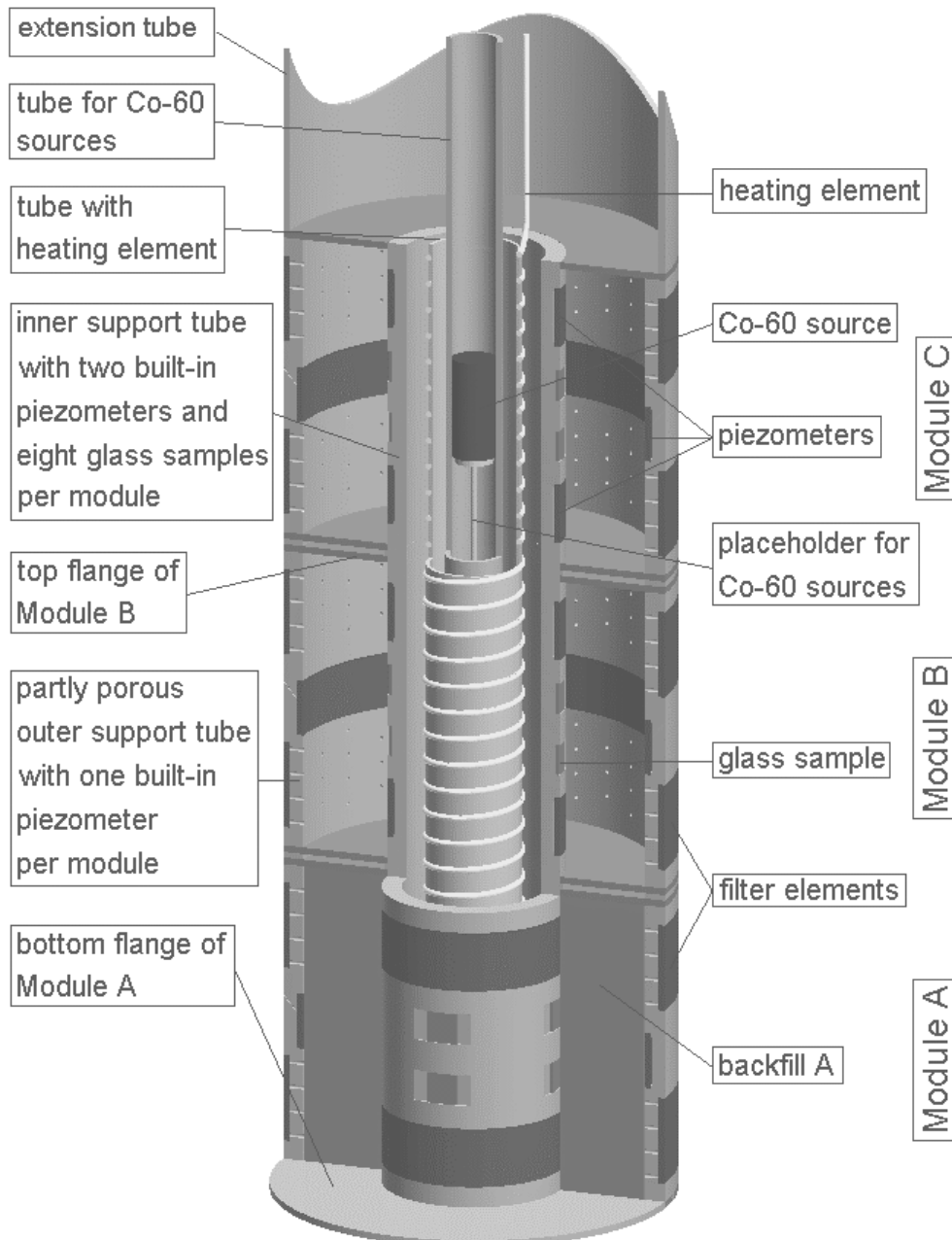
Figure 1.1   Test tube with ^{60}Co source /VAL 97/

The following investigations are 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 and
  - 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 release from the different backfill materials in contact with air and inert atmosphere in the natural dry and wet stage are determined at temperatures up to 90 °C. In addition, petrophysical parameters such as porosity, gas permeability, and gas diffusivity are 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 are determined.

In this report, the results obtained during the period of investigation from 1996 to 2000 are presented.

3   Methods

3.1   Measurement of gas release from the different backfill materials

Within the frame of the laboratory programme, the gas generation and gas release from the three different backfill materials were investigated under defined physico-chemical conditions in gas-tight sealed glass ampoules with a volume of 500 ml, as shown in figure 3.1. Through the injection tube at the top, 100 grams of the backfill material were transferred into the ampoule in the dry stage. A valve with septum was then attached to the injection tube. The residual volume of one-third of the ampoules was filled with laboratory air. The other ampoules were evacuated to about 100 Pa and refilled again to atmospheric pressure, one-third of these were filled with pure nitrogen, the other third were filled with a special glove box atmosphere (99.6 % argon, 0.4 % carbon dioxide, and less than 0.0003 % oxygen). Clay formation water (wet stage) was then added with a syringe by way of the septum on the injection tube to one-half of the ampoules. About 10.5 ml was added to the dried Boom clay (Backfill A), 10.7 ml was added to the FoCa clay with sand and graphite (Backfill B), and 13.2 ml 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 precompacted backfill blocks, which are installed in the modules of the test tube. The ampoules were sealed gas-tight after fill-ing. For statistical reasons, at least 3 replicates of each set of conditions were prepared and investigated.

Since the influence of handling in the open air was not known, the backfill material was injected into the ampoules immediately from the storage containers. The material was not homogenised, since this would have required drying. Furthermore, intensive con-tact with the open air would have occurred during homogenisation; this could cause release of adsorbed or trapped gases and oxidation of unstable components. Since the material was not homogenised, differences may occur between similar ampoules.

For gas generation and release from the backfill material, the gas-tight sealed am-poules were stored for 100 days in an oven at temperatures of 40 or 90 °C.
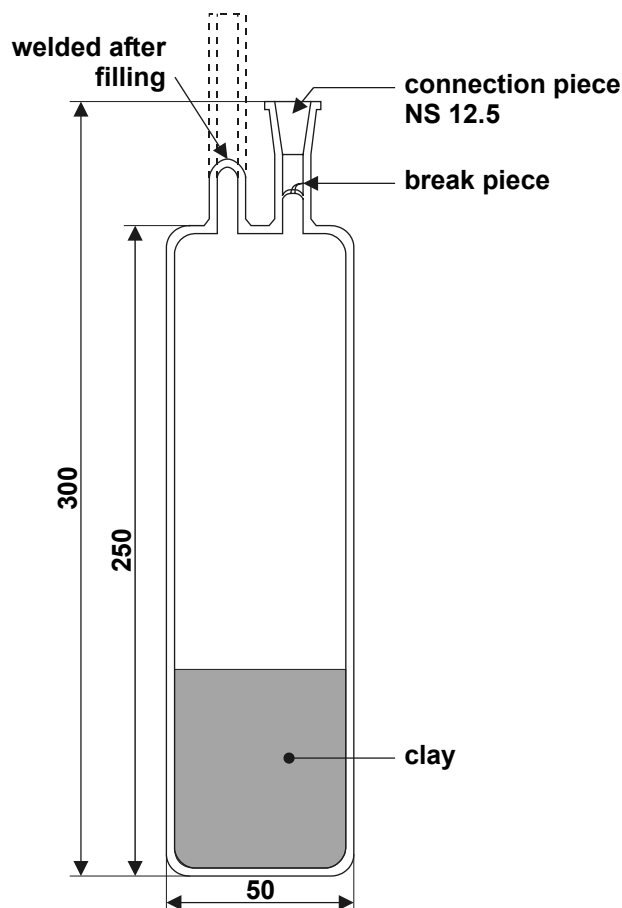
Figure 3.1   Ampoule for the investigation of generation and release of gases from the different backfill materials as a result of elevated temperature

After 100 days of storage at the envisaged temperature, 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 then 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 the nitrogen.
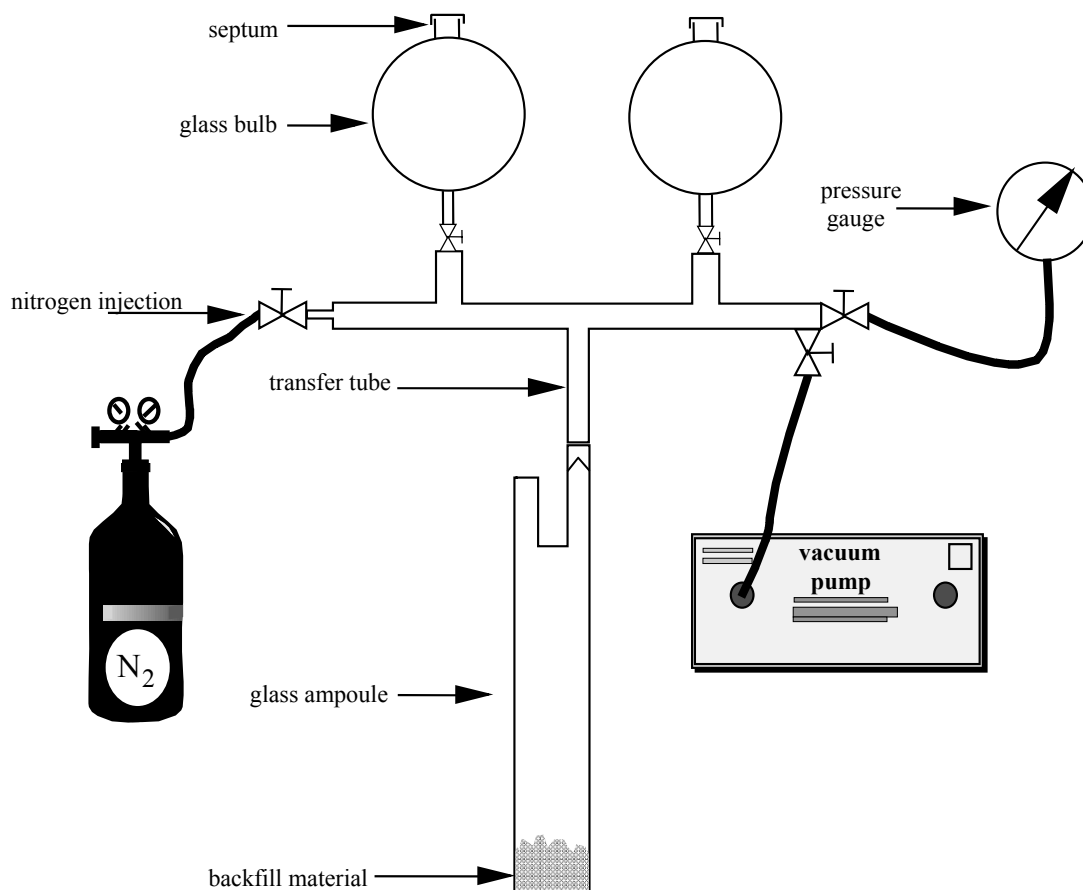

septum

glass bulb

pressure gauge

nitrogen injection

transfer tube

N₂

vacuum pump

glass ampoule

backfill material

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

The GC system consists of four independent GC 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)

3.2   Diffusivity, permeability, and porosity of the different backfill materials

Gas diffusion was determined on compacted samples with a thickness of 10 mm in the air-dry stage and in the water-saturated stage with the use of a special sample holder, as shown in figure 3.3.

For the preparation of the samples, the sample holder was closed with the bottom lid at one end. The amount of backfill material necessary for obtaining a sample with a thickness of 10 mm, a diameter of 50 mm, and a dry density of 1880 kg/m³ for backfill A and B, and 1620 kg/m³ for backfill C, respectively, was transferred to the open-site sample holder. The original water content of the different backfill materials in the mass content range between 4 and 12 per cent was taken into account for determining the amount of

backfill material necessary for obtaining the desired dry density. The material was then compacted to the defined height with a hydraulic press. The necessary forces were 30 kN (15.3 MPa) for backfill materials A and B and 18 kN (9.2 MPa) for backfill C. In order to ensure a uniform distribution of the gases at both ends of the sample, stainless steel filter frits were placed on the pistons of the sample holder.
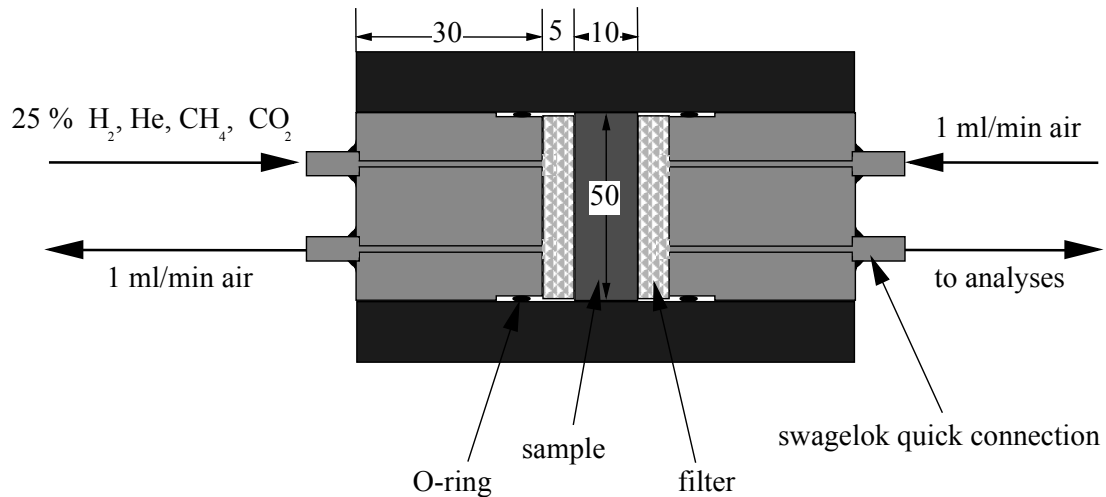

Figure 3.3   Sample holder for determining the gas diffusivity on different backfill materials

For determining the gas diffusivity, the sample holder was mounted horizontally, and the front end of the sample was purged with 3 ml of two different gas mixtures. One mixture consisted of hydrogen, helium, methane and carbon dioxide at contents of 25 per cent each, and the other consisted of helium, neon, argon and krypton at the same contents. The back end of the sample was purged with laboratory air or with pure nitrogen. Since the gas flows were equal at both ends and the configuration was symmetrical, no pressure gradient occurred between the two ends of the sample; this is a necessary boundary condition for determining the diffusivity. In the gas flow at the back end, the gas concentrations of the purging components at the front end were determined with the use of a mass spectrometer.

For determining the gas permeability of the same sample, the gas exits were closed at both ends of the sample holder, and nitrogen was supplied through the gas inlet at the front end at a pressure of 0.01 MPa in the case of the dry stage or 0.9 MPA for the water-saturated stage. A gas flow meter was connected to the open outlet at the back

end, and the gas flow caused by the pressure gradient between the two ends of the sample was determined.

After these measurements in the dry stage, both ends of the sample were rinsed with 50 ml of formation water. This purging operation was repeated three times within 24 hours and resulted in water saturation of the sample. The measurements of diffusivity and permeability were then repeated in a manner similar to that for the dry stage, but with water-saturated gases at both ends in order to avoid drying of the sample. Finally, the samples were pressed out of the sample holder and weighed. From the difference in weight between the air-dry and water-saturated stages, which results from adsorption of water, the porosity was calculated for the air-dry stage of the compacted samples. The air-dry backfill material already contains adsorbed water on the internal surface. If this amount of water is added to the amount which was necessary for flooding, the total porosity can be calculated.

The water content of the air-dry backfill material was determined with a thermogravimeter by heating 100 mg to 105 °C in a dry nitrogen atmosphere, until the weight no longer changed. The loss in weight was interpreted as the water content of the sample.

The diffusivities of the different gas components were calculated from Fick's first law /JOS 72/:

$$D = \frac{J \cdot l}{\Delta c \cdot A}$$

with:

D	diffusion coefficient	m^2/s
J	diffusion rate $= j \cdot c_{II}$	g/s
j	purging rate at the back end	m^3/s
c_{II}	concentration of the gas component at the back end	g/m^3
l	length of the sample	m
Δc	concentration gradient between both ends of the sample	g/m^3
A	cross-sectional area of the sample	m^2

The permeability was calculated with the use of Darcy's law for compressible fluids /LAN 82/:

$$k_g = \frac{2 \cdot q_g \cdot \mu_g \cdot l \cdot p_0}{A \cdot (p_1^2 - p_0^2)}$$

with:

k_g	gas permeability	m²
q_g	flow rate of the gas	m³/s
p_1	injection gas pressure	Pa
p_0	air pressure	Pa
μ_g	dynamic viscosity of the gas	Pa·s
l	length of the sample	m
A	cross-sectional area of the sample	m²

The porosity was calculated from the following equation:

$$\Phi = \frac{V_{por}}{V_b},$$

Φ	porosity	
V_{pro}	pore volume of the sample which is equivalent to the amount of adsorbed water with a density of 1000 kg/m³	m³
V_b	bulk volume of the sample	m³

The results of the investigations are summarised in table 4.2. Data for the various gas constants were taken from /DAN 92/, /KOH 86/, /LAI 76/, /LID 94/, and /LIN/.

3.3   Internal surface

The internal surface of the different backfill materials was determined by the BET nitrogen adsorption method (S. Brunauer, P. H. Emmett and E. Tellert) /KEL 82/. The adsorption isotherm at the boiling temperature of liquid nitrogen was determined by this method for the pressure ratio p/p_0 in the range between 0.05 and 0.3. (p is the actual nitrogen pressure, and p_0 is the pressure at gas saturation in the sample container.) In this range, the plot of the isotherm (BET plot) is a straight line and is proportional to the internal surface.

For determining the internal surface, the amount of nitrogen necessary for a defined pressure ratio was measured for both the sample container and an identical container for comparison. With the knowledge of the free gas volumes of both containers and the amount of injected gas, the amount of gas adsorbed by the sample was calculated as a function of the pressure ratio. Since the amount of adsorbed gas is proportional to the adsorbing internal surface and the area occupied by an adsorbed gas molecule, the internal surface is given by /LAN 82/

$$S = f \cdot L \cdot \frac{V_m}{V_0}$$

with:

S	internal surface	m^2
f	area occupied by one molecule	m^2
	for nitrogen $f = 16.2 \cdot 10^{-20}$	m^2
L	Loschmidt's constant	1/mol
V_m	sorption volume for a monomolecular layer	m^3
V_0	molar volume of the gas	m^3/mol

In general, the specific internal surface per unit mass $\dfrac{S}{m}$ is calculated.

The measurements of the internal surfaces of the different backfill materials were performed by the "Institut für Angewandte Geowissenschaften der Technischen Universität Berlin".

3.4   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 are routed 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 pressure 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. All valves were then 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.

In the GRS laboratory in Braunschweig, the content of the sampling container was transferred to a 500 ml stainless steel container which was flooded afterwards with nitrogen to atmospheric pressure. In order to remove the air and the adsorbed gases from that steel container it was evacuated and flooded three times before transferring the water.

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. With the use of a syringe, 100 ml of the gas was 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. Then it was closed and stored again 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.

3.5   In situ permeability measurements

The aim of the in situ permeability measurements in both the backfill and the surrounding Boom clay of the CORALUS tube 1 was to characterise the flow processes in the highly water-saturated materials and to detect changes induced by heating. The following tests were performed:

- Measurement of the effective permeability of the Boom clay host rock to water prior to heating

- Measurement of the effective permeability of the Boom clay host rock to gas at a distance of 0.5 m from the CORALUS tube 1 prior to, during, and after heating

- Measurement of the effective permeability of the different backfill materials to gas towards the end of the heating period

- Determination of the permeability of the different backfill materials to liquid before and during the heating period

For the measurements in the boom clay, a piezometer probe was installed at a distance of about 0.5 m from the inactive CORALUS test assembly at the same borehole depth in June, 1998. It consists of a steel pipe with two ring-shaped piezometers which serve as nitrogen injection intervals (see figure 3.4). Sealing of the probe in the borehole is achieved by the convergence of the surrounding clay. From each piezometer two steel tubes lead to the connecting panel in the drift. Two tubes are needed for each piezometer, since the formation water has to be removed from the piezometer before a gas permeability measurement can be started. This is done by injecting nitrogen while the return tube is left open, in order to press the water out. A transducer cabinet with pressure transducers, flowmeters, and a datalogger was installed in October, 1998. The system is represented diagrammatically in figure 3.5.
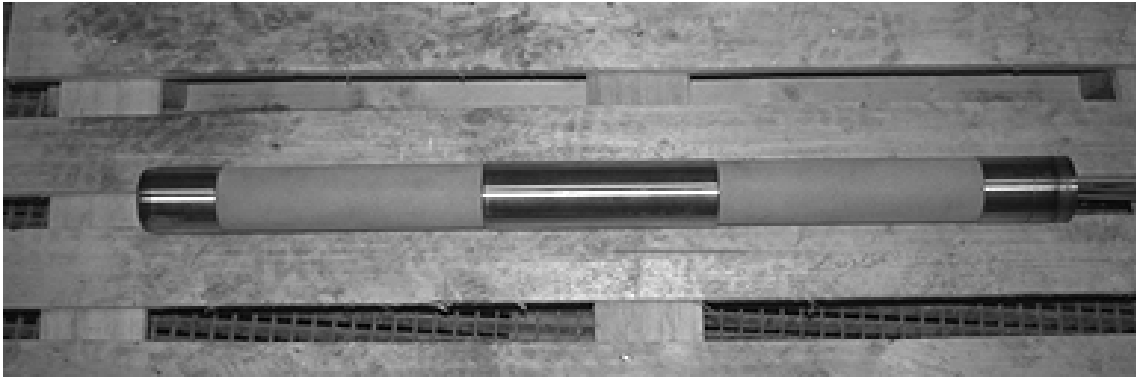
Figure 3.4   Piezometer probe installed in the boom clay

At the time of installation of the transducer cabinet, a fluid overpressure of about 5.5 and 6 bar had built up in the upper and lower piezometer, respectively. Since there was no overpressure in the connecting tubes between the transducer cabinet and the connecting panel, the installation of the cabinet resulted in a pressure draw-down. Subsequently, the pressure started to increase.

The procedure of connecting the transducer cabinet to the probe can be regarded as a pressure draw-down/build-up test, which is common in oil-field permeability testing /EAR 77/. 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 4.5.

In order to determine the effective permeability of the formation to gas under the present saturation conditions, and especially changes in permeability due to heating, gas injection tests with nitrogen were performed in the lower piezometer of the probe prior to heating, at the end of the heating phase, when the temperature at the probe had risen to about 34 °C, and after cool-down. Prior to each gas injection, the piezometer was purged with nitrogen. From the pressure development during the injection and the subsequent shut-in phase, the effective permeability to gas was again estimated with the use of the Weltest code.
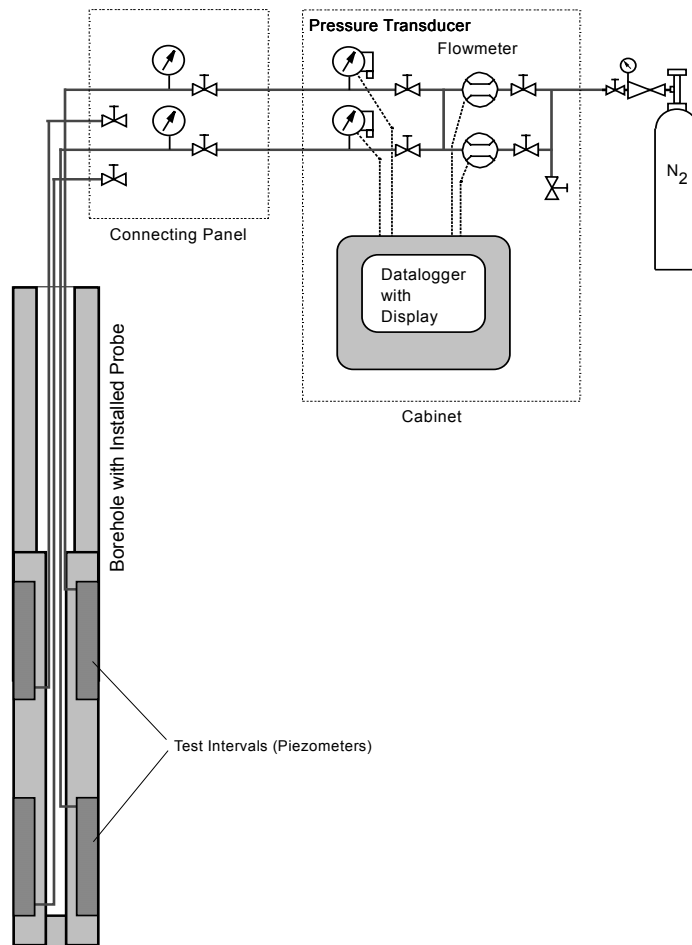
Figure 3.5   Overview of the permeability measurement system

Gas injection tests in the backfill were possible only at the end of the heating period on 13th April, 1999. In each of the three backfill bodies, a gas injection test was performed in the lower central piezometer of the CORALUS tube (see figure 1.1). The temperature at the piezometers was about 90 °C.

Prior to and during the heating period, several samples of the interstitial solution in the backfill were taken from the various piezometers installed in the CORALUS test tube (see section 3.4). Sampling resulted in a pressure draw-down with a subsequent pressure build-up phase, which can be used for determining the backfill permeability in the same way as the pressure build-up test in the piezometer probe installed in the Boom clay. Such evaluations were tried successfully (see section 4.5).

4   Results

In the present chapter, the results of the laboratory and in situ measurements on the three different backfill materials:

- dried Boom clay (backfill A),

- 60 per cent FoCa clay with 35 per cent sand and 5 per cent graphite (backfill B) (mass contents),

- 95 per cent FoCa clay with 5 per cent glass powder (backfill C),

and on the solid Boom clay are presented. The mineralogical composition of the two clay materials are (information of SCK-CEN)

Boom clay:

illite	20 – 30 %
smectite	10 – 20 %
chlorite	5 – 20 %
kaolinite	20 – 30 %
organic matter	5 – 10 %

and accessory minerals, such as quartz, feldspar, calcite, pyrite, siderite

FoCa clay is a Ca-bentonite:

mixture of kaolinite and smectite	86 %
quartz	6 %
goethite	6 %
calcite	1.4 %
hematite	0.2 %
gypsum	0.4 %

4.1   Measurements of gas release from the different backfill materials

The results (mean values) of the investigation on gas generation and release from the different backfill materials, as described in section 3.1, are shown in figures 4.1 to 4.4 and in table 4.1. For better comparability, the results are normalised with respect to litres per 1000 kg dry material.

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Hydrogen was released in significant amounts only from the FoCa clay samples (backfill B and C) up to 9 l gas per 1000 kg of backfill. In the ampoules with Boom clay, hydrogen was detected up to 0.17 l per 1000 kg only when a glove box atmosphere was present in the residual volume.

Methane was released in comparatively small amounts up to 0.011 l per 1000 kg in the FoCa clay samples (backfill B and C); the value was higher by a factor of 10 (up to 0.08 l per 1000 kg) in the Boom clay sample (backfill A). The temperature, the additional formation water, and the atmosphere (inert or aerobic) do not seem to have a significant influence on the generation of methane. Since the Boom clay, in contrast to the FoCa clay, contains a significant amount of organic matter (3 – 5 %) the release of methane could be explained by decomposition of this matter.

Carbon dioxide is the only gas which was released in significant amounts. At a temperature of 90 °C, up to 559 l per 1000 kg were detected in the Boom clay samples, and up to 159 l per 1000 kg in the FoCa clay samples. Again, the atmosphere does not seem to have a significant influence on the generation and release of this component, whereas the temperature does exert a significant influence. In the dry version with air in the residual volume, the carbon dioxide release is comparatively low (up to 73 l per 1000 kg). This component is apparently adsorbed on the internal surface of the clay. In the wet stage, water is already adsorbed on the internal surface of the clay, and the solubility of carbon dioxide in water at 40 and 90 °C is comparatively low. Therefore, this component is desorbed into the residual volume of the ampoule. If the temperature is increased from 40 to 90 °C, the amount of released carbon dioxide increases by a factor of 10 to 20.

Since the amount of released carbon dioxide is affected by the temperature, but not by the atmosphere (inert or aerobic), it is most likely that this component 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 per cent of calcite ($CaCO_2$) (mass content), which could be decomposed thermally in the presence of the synthetic formation water. Additional investigations on this subject are necessary.
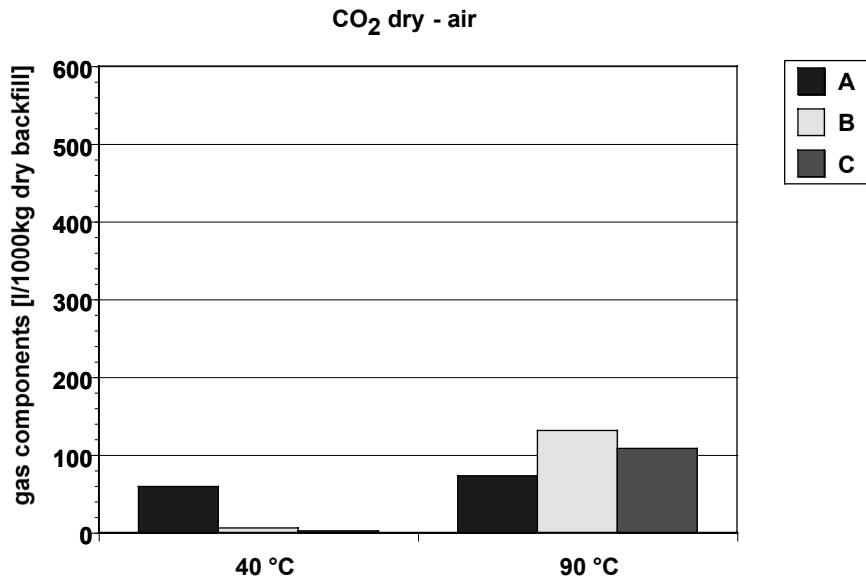
CO$_2$ dry - air

Figure 4.1   Release of carbon dioxide from the different backfill materials in the natural dry stage with air in the residual volume of the ampoules at 40 and 90 °C; Boom clay (A), FoCa clay with sand and graphite (B), FoCa clay with glass powder (C)
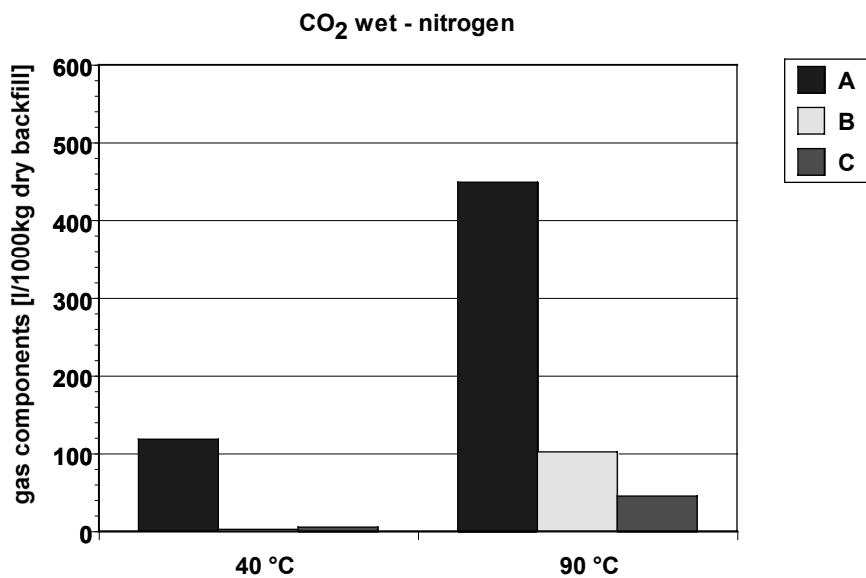

CO$_2$ wet - nitrogen

Figure 4.2   Release of carbon dioxide from the different backfill materials with additional formation water and nitrogen in the residual volume of the ampoules at 40 and 90 °C; Boom clay (A), FoCa clay with sand and graphite (B), FoCa clay with glass powder (C)
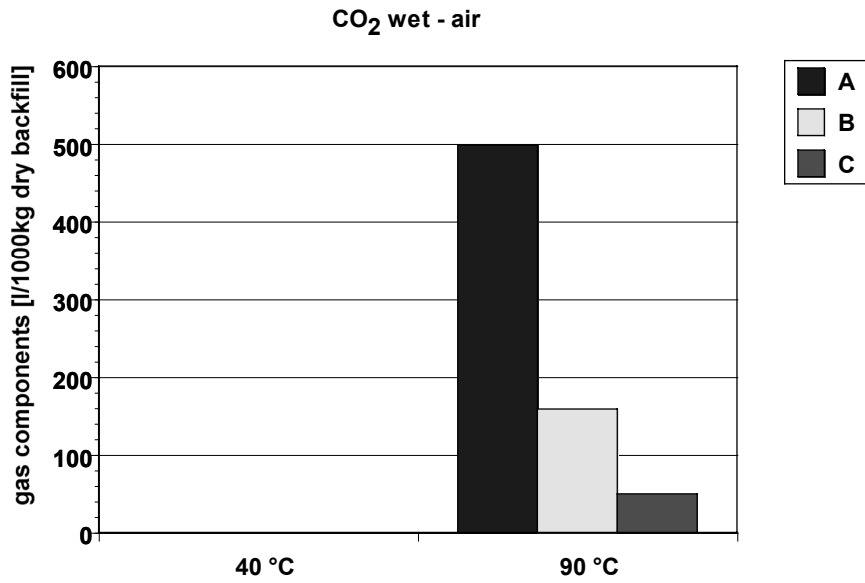
CO$_2$ wet - air

Figure 4.3   Release of carbon dioxide from the different backfill materials with additional formation water and air in the residual volume of the ampoules at 40 and 90 °C; Boom clay (A), FoCa clay with sand and graphite (B), FoCa clay with glass powder (C)
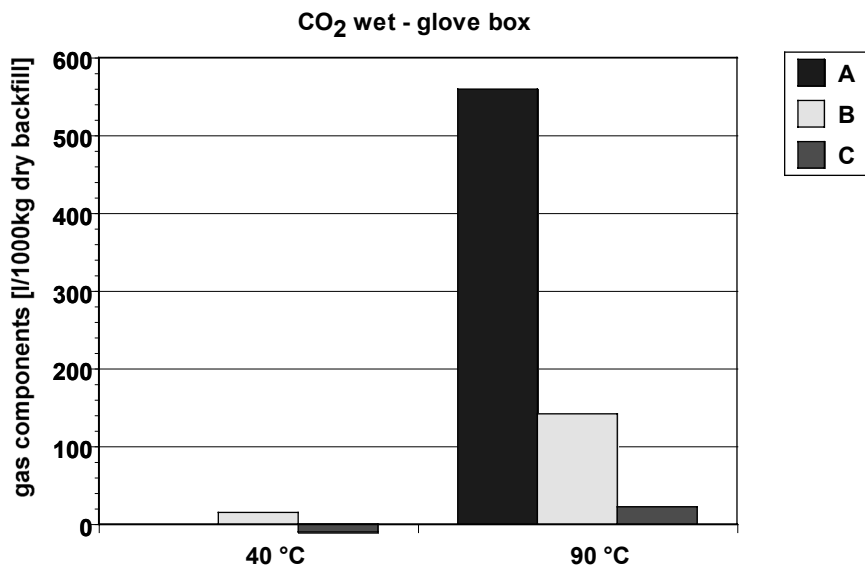

CO$_2$ wet - glove box

Figure 4.4   Release of carbon dioxide from the different backfill materials with additional formation water and glove box atmosphere* in the residual volume of the ampoules at 40 and 90 °C; Boom clay (A), FoCa clay with sand and graphite (B), FoCa clay with glass powder (C)

Table 4.1   Mean values for the components hydrogen, methane, and carbon dioxide released from the different backfill materials in the dry and wet stage with air, nitrogen or glove box atmosphere* in the residual volume of the ampoules for 40 and 90 °C; Boom clay (A), FoCa clay with sand and graphite (B), FoCa clay with glass powder (C)

| T, °C | stage | atmosphere | hydrogen, l /1000kg | | |
| | | | backfill | | |
			A	B	C
40	dry	air	n. m.	n. m.	n. m.
40	wet	nitrogen	n. m.	0.9	2.0
40	wet	glove box*	false	9.0	1.7
90	dry	air	n. m.	n. m.	0.6
90	wet	air	n. m.	n. m.	2.4
90	wet	nitrogen	n. m.	2.0	7.0
90	wet	glove box*	0.17	9.0	6.0
T, °C	stage	atmosphere	methane, l /1000kg		
			backfill		
			A	B	C
40	dry	air	0.01	0.007	0.000
40	wet	nitrogen	0.02	0.005	0.003
40	wet	glove box*	false	0.020	0.006
90	dry	air	0.08	0.008	0.007
90	wet	air	0.07	0.009	0.000
90	wet	nitrogen	0.06	0.005	0.007
90	wet	glove box*	0.07	0.008	0.011
T, °C	stage	atmosphere	carbon dioxide, l / 1000kg		
			backfill		
			A	B	C
40	dry	air	59.0	6.0	2.0
40	wet	nitrogen	118.0	2.0	4.9
40	wet	glove box*	false	15.0	- 10.2
90	dry	air	73.0	131.0	108.0
90	wet	air	498.0	159.0	50.0
90	wet	nitrogen	449.0	102.0	45.0
90	wet	glove box*	559.0	142.0	22.0

*   glove box atmosphere = 99.6 % argon,
     0.4 % carbon dioxide and less than 0.0003 % oxygen
     m. n. = not measurable

The negative values for carbon dioxide in backfill C at 40 °C result from adsorption of this component from the glove box atmosphere on the internal surface of the clay. The ampoule with backfill A stored at 40 °C with a glove box atmosphere took up air before

or during welding. This resulted in a falsification, and the results are therefore not mentioned.

4.2 Diffusivity, permeability and porosity of the different backfill materials

The results of the investigations on diffusivity, permeability, and porosity of the different backfill materials, as described in section 3.2, are summarised in table 4.2.

The diffusivities of the different gases at room temperature (20 °C) in the air-dry stage of the backfill materials A, B, and C are in the range between $100 \cdot 10^{-9}$ and $400 \cdot 10^{-9}$ m^2/s. No significant differences were observed among the different backfill materials and the various gas components. The values for the samples CD4, CD5, and CD6 are lower than the values for all other samples by a factor of 10 to 20 under the same conditions. The reason for this difference is not yet known. These samples should not be taken into consideration for comparisons and for determining the influence of the different parameters.

In the air-dry stage of the backfill materials, the diffusivity does not seem to be influenced by the temperature. Variations are within the limits of error.

In the flooded stage of the backfill material, the diffusivity of the gases hydrogen, helium, methane, neon, argon, and krypton at 20 and 40 °C is below the detection limit of $0.1 \cdot 10^{-9}$ m^2/s. Only the diffusivity of carbon dioxide is above the detection limit; its value is in the range from 0.1 to $0.6 \cdot 10^{-9}$ m^2/s. This difference is due to the fact that the solubility of carbon dioxide in water at 20 °C is 0.087 litre per kg of water, whereas the range of solubility for the other gases is between 0.003 and 0.018 litre per kg of water. Since the amount of carbon dioxide dissolved in the water is much greater at the front end of the sample, it diffuses much faster through the sample, and much greater amounts of this gas are consequently released at the back end. The result is a correspondingly higher diffusivity value.

The diffusivities at 90 °C in the flooded stage of all three backfill materials are in the range from $0.1 \cdot 10^{-9}$ to $4 \cdot 10^{-9}$ m^2/s. The reason for the higher diffusivities might be the fact that at 90 °C the pore volume of the samples is filled with water not only in the liquid phase, but also in the vapour phase. Diffusion therefore occurs in the gas-filled pore volume, rather than in the water-filled pore volume.

The samples CD13, CD14, and CD15 were purged at the front ends with the mixture of 25 per cent each of helium, neon, argon, and krypton. The back ends were purged with pure nitrogen, in order to check whether additional carbon dioxide is released from the samples. In the air-dry stage and in the water-saturated stage of the sample, the volume content of carbon dioxide in the nitrogen purging flow at the back ends was below 100 vpm (0.01 per cent). This carbon dioxide originated from laboratory air, which has a volume content of carbon dioxide in the range of 500 vpm (0.05 per cent). This result indicates that the high diffusivity values obtained for carbon dioxide in the water-saturated stage of the samples are not falsified by the release of carbon dioxide from the backfill material.

With a value in the order of 10^{-13} m^2, the gas (nitrogen) permeability of the different backfill materials in the air-dry stage is comparatively high and does not vary significantly. The backfill materials in the air-dry stage represent an open system in which gases can diffuse and migrate without significant resistance. Measurements of gas permeability in the flooded stage, which were performed up to a gas injection pressure of 0.9 MPa (9 bar), have not indicated any gas flow within a period of 24 hours. This means that the backfill materials are gas-tight up to 0.9 MPa. With the present equipment, it was not possible to increase the injection gas pressure above 0.9 MPa. Modification of the equipment would be necessary for determining the break-through pressure for gas.

The porosity of the compacted samples in the air-dry stage, which is relevant for gas permeability and gas diffusion in that stage, is in the range between 15.0 and 26.7 per cent. Again, there are no significant differences among the three backfill materials. This corresponds with the fact that gas diffusivity and gas permeability are not significantly different in the backfill materials.

The total porosity of the absolute dry (gas-filled pore volume) or flooded (water-filled pore volume) compacted samples is in the range between 29.1 and 43.3 per cent, with no significant differences in the three backfill materials. This porosity and its distribution are decisive for the gas break-through pressure and two-phase flow in the partly saturated stage of the backfill material.

Table 4.2   Diffusivity, gas permeability, and porosity of the different compacted backfill materials in the air-dry and water-flooded stages at temperatures of 20, 40, and 90 °C

Nr.	back-fill	temp. [°C]	condition	gas flow front end	gas flow back end	diff. H_2	diff. He	diff. CH_4	diff. CO_2	diff. He	diff. Ne	diff. Ar	diff. Kr	permeability air dry [10^{-13} m²]	porosity air dry %	porosity total %
CD1	A	20	air dry	H_2, He, CH_4, CO_2	laboratory air	395	402	263	248					1.67	26.7	34.9
			water flooded	H_2, He, CH_4, CO_2	laboratory air	<0.1	<0.1	<0.1	0.6							
CD2	B	20	air dry	H_2, He, CH_4, CO_2	laboratory air	275	292	189	184					1.30	15.0	29.1
			water flooded	H_2, He, CH_4, CO_2	laboratory air	<0.1	<0.1	<0.1	0.5							
CD3	C	20	air dry	H_2, He, CH_4, CO_2	laboratory air	146	151	121	127					1.04	24.4	43.3
			water flooded	H_2, He, CH_4, CO_2	laboratory air	<0.1	<0.1	<0.1	0.6							
CD4	A	20	air dry	H_2, He, CH_4, CO_2	laboratory air	21	20	17	18							
			water flooded	H_2, He, CH_4, CO_2	laboratory air	<0.1	<0.1	<0.1	0.2							
CD5	B	20	air dry	H_2, He, CH_4, CO_2	laboratory air	19	19	16	16							
			water flooded	H_2, He, CH_4, CO_2	laboratory air	<0.1	<0.1	<0.1	0.2							
CD6	C	20	air dry	H_2, He, CH_4, CO_2	laboratory air	12	13	11	12							
			water flooded	H_2, He, CH_4, CO_2	laboratory air	<0.1	<0.1	<0.1	0.1							
CD7	A	20	air dry	H_2, He, CH_4, CO_2; He, Ne, Ar, Kr	laboratory air	119	176	166	162	127	135	136	118	1.85		
		40	air dry	H_2, He, CH_4, CO_2; He, Ne, Ar, Kr	laboratory air	133	169	174	147	116	122	151	113			
		90	air dry	H_2, He, CH_4, CO_2; He, Ne, Ar, Kr	laboratory air	220	234	229	212	157	88	178	291			
CD8	B	20	air dry	H_2, He, CH_4, CO_2; He, Ne, Ar, Kr	laboratory air	129	206	162	142	134	134	132	116	1.43		
		40	air dry	H_2, He, CH_4, CO_2; He, Ne, Ar, Kr	laboratory air	144	166	145	123	106	102	102	92			
		90	air dry	H_2, He, CH_4, CO_2; He, Ne, Ar, Kr	laboratory air	255	225	225	218	122	123	125	115			
CD9	C	20	air dry	H_2, He, CH_4, CO_2; He, Ne, Ar, Kr	laboratory air	352	435	281	242	182	174	164	136	1.29		
		40	air dry	H_2, He, CH_4, CO_2; He, Ne, Ar, Kr	laboratory air	63	83	101	265	120	118	139	106			
		90	air dry	H_2, He, CH_4, CO_2; He, Ne, Ar, Kr	laboratory air	284	312	298	283	80	92	89	87			

Diffusivity values are in $[10^{-9} \cdot m^2/s]$; permeability in $[10^{-13} \cdot m^2]$; porosity in %.

Nr.	back-fill	temp. [°C]	condition	gas flow front end	gas flow back end	diff. H_2	diff. He	diff. CH_4	diff. CO_2	diff. He	diff. Ne	diff. Ar	diff. Kr	perm. air dry	poros. air dry	poros. total
CD10	A	20	water flooded	H_2, He, CH_4, CO_2	laboratory air	<0.1	<0.1	<0.1	0.1					25.2		33.5
				He, Ne, Ar, Kr						<0.1	<0.1	<0.1	<0.1			
		40		H_2, He, CH_4, CO_2		0.3	0.3	0.3	0.1							
				He, Ne, Ar, Kr						<0.1	<0.1	<0.1	<0.1			
		90		H_2, He, CH_4, CO_2		<0.1	<0.1	<0.1	<0.1							
				He, Ne, Ar, Kr						0.4	0.3	0.7	<0.1			
CD11	B	20	water flooded	H_2, He, CH_4, CO_2	laboratory air	<0.1	<0.1	<0.1	<0.1					14.6		28.7
				He, Ne, Ar, Kr						<0.1	<0.1	<0.1	<0.1			
		40		H_2, He, CH_4, CO_2		<0.1	<0.1	<0.1	<0.1							
				He, Ne, Ar, Kr						<0.1	<0.1	<0.1	<0.1			
		90		H_2, He, CH_4, CO_2		0.3	0.4	0.4	0.1							
				He, Ne, Ar, Kr						0.2	0.2	0.2	<0.1			
CD12	C	20	water flooded	H_2, He, CH_4, CO_2	laboratory air	<0.1	<0.1	<0.1	<0.1					27.4		46.3
				He, Ne, Ar, Kr						<0.1	<0.1	<0.1	<0.1			
		40		H_2, He, CH_4, CO_2		<0.1	<0.1	<0.1	<0.1							
				He, Ne, Ar, Kr						<0.1	<0.1	<0.1	<0.1			
		90		H_2, He, CH_4, CO_2		3	4	3	1							
				He, Ne, Ar, Kr						1	2	1	<0.1			
CD13	A	20	air dry	He, Ne, Ar, Kr	N_2					206	201	192	174	24.0		32.2
			water flooded	He, Ne, Ar, Kr	N_2					<0.1	0.1	0.1	<0.1			
CD14	B	20	air dry	He, Ne, Ar, Kr	N_2					200	194	186	168	11.9		26.0
			water flooded	He, Ne, Ar, Kr	N_2					<0.1	0.1	0.1	<0.1			
CD15	C	20	air dry	He, Ne, Ar, Kr	N_2					157	149	127	120	26.4		45.4
			water flooded	He, Ne, Ar, Kr	N_2					<0.1	0.6	0.8	<0.1			

Legend:
Backfill A: dried Boom clay
Backfill B: 60 % FoCa clay, 35 % sand, 5 % graphite
Backfill C: 95 % FoCa clay, 5 % glass powder

4.3 Internal surface

The internal surface of the different backfill materials was determined by the BET method by the "Institut für Angewandte Geowissenschaften der Technischen Universität Berlin" /DEB 99/. The results for the uncompacted powders are

dried Boom Clay (backfill A)   20.8 to 21.8 m^2/g

FoCa clay with sand and graphite (backfill B)   9.5 to 10.0 m^2/g

FoCa clay with glass powder (backfill C)   12.1 to 12.6 m^2/g

The internal surface is of no importance for gas and water migration, but it is decisive for the sorption and migration of corrosion products and released radionuclides. Therefore, it is worthwhile to perform these measurements on the compacted backfill materials which are installed in the different modules of the test boreholes.

4.4 Gases dissolved in the interstitial water

The gases dissolved in the formation water of the different backfill materials are listed in table 4.3.

Samples of the real clay water (RCW), which was injected into the different modules, were taken from the storage container on 10th February, 1999. Water samples were taken from the different piezometers of modules A, B, and C prior to heating on 4th, 10th, and 25th February. Electrical heating of the CORALUS tube 1 started on 25th February, 1999. During the heating phase, samples were taken from all piezometers on 12th April, 1999. Analyses were performed in the GRS laboratory as described in section 3.4. The only gases that could be detected were oxygen, carbon dioxide, and methane.

Table 4.3   Gases dissolved in the formation water of the different piezometers

Date of sampling	Piezometer	Gas Content, l/ 1000kg		
		[2] O_2 + Ar	CO_2	CH_4
10.02.99	RCW-Module A	362	68	0.05
10.02.99	RCW-Module B	560	68	0.06
10.02.99	RCW-Module C	457	67	0.06
13.01.99	A1	[1]	[1]	[1]
04.02.99	B1	129	52	0.19
04.02.99	C1	105	130	traces
10.02.99	A2	81	124	traces
10.02.99	B2	220	77	0.57
10.02.99	C2	277	107	0.07
25.02.99	A3	130	229	17.4
25.02.99	B3	152	39	5.3
25.02.99	C3	398	36	2.7
12.04.99	A1	25	165	8.2
12.04.99	B1	34	67	1.1
12.04.99	C1	105	111	1.8
12.04.99	A2	209	156	1.5
12.04.99	B2	208	98	0.54
12.04.99	C2	212	148	0.36
12.04.99	A3	60	221	8.4
12.04.99	B3	105	111	1.8
12.04.99	C3	89	96	0.92

[1] erroneous measurement

[2] As the gas chromatography system can not distinguish between oxygen and argon the values represent the concentration of both gases.

The real clay water (RCW) injected into the backfill contained between 362 and 560 l of oxygen/argon per 1000 kg; that is, it was saturated with oxygen/argon. The content of carbon dioxide ranged between 67 and 68 l/1000 kg. Methane was found only in traces (less than 0.1 l/1000 kg), and the hydrogen content was below the detection limit of 0.1 l/1000 kg.

The water which was extracted from the piezometers prior to heating had a lower oxygen/argon content ranging between 81 and 398 l/1000 kg. The carbon dioxide content increased up to 229 l/1000 kg, and methane up to 17 l/1000 kg. The hydrogen content remained below the detection limit. This means that oxygen from the RCW was consumed, while carbon dioxide was generated.

After switching on the heaters of CORALUS tube 1, water samples were taken from all piezometers for analysis of the gas content on 12th April, 1999. Only one sample (pie-

zometer B2) contained a detectable quantity of hydrogen, with 0.3 l/1000 kg; in all other samples, the hydrogen content was still below the detection limit. As expected, the content of the other gases dissolved in the water extracted from the piezometers did not show a significant dependence on heating. The time interval between the start of heating and sampling was obviously too short for reaching an equilibrium with respect to the temperature, as well as the generation and dissolution of gases.

The results of the investigations on CORALUS tube 1 can be summarised as follows:

- The methods of sampling and analysis of the gases dissolved in the extracted backfill water proved to be well suited for the purpose.

- The elapsed time was not long enough for reaching an equilibrium between gas generation and dissolution in the formation water, regardless of whether at ambient or at elevated temperature.

- The water to be injected into the piezometers should not contain oxygen or any other gases which undergo reactions or falsify the results.

- For the measurements in CORALUS tubes 2, 3, and 4, much longer time intervals are necessary for reaching a steady state, even at ambient temperature.

4.5   In situ permeability measurements

4.5.1   Permeability of the Boom clay formation to water

When the transducer cabinet with pressure transducers, flowmeters, and a datalogger were installed in October, 1998, a fluid overpressure between 5.5 and 6 bar had built up in the piezometers of the probe located in the Boom clay. Connection of the cabinet to the probe resulted in a pressure draw-down. Subsequently, the pressure started rising again. The recorded pressure curves for the two piezometers are shown in figure 4.5.
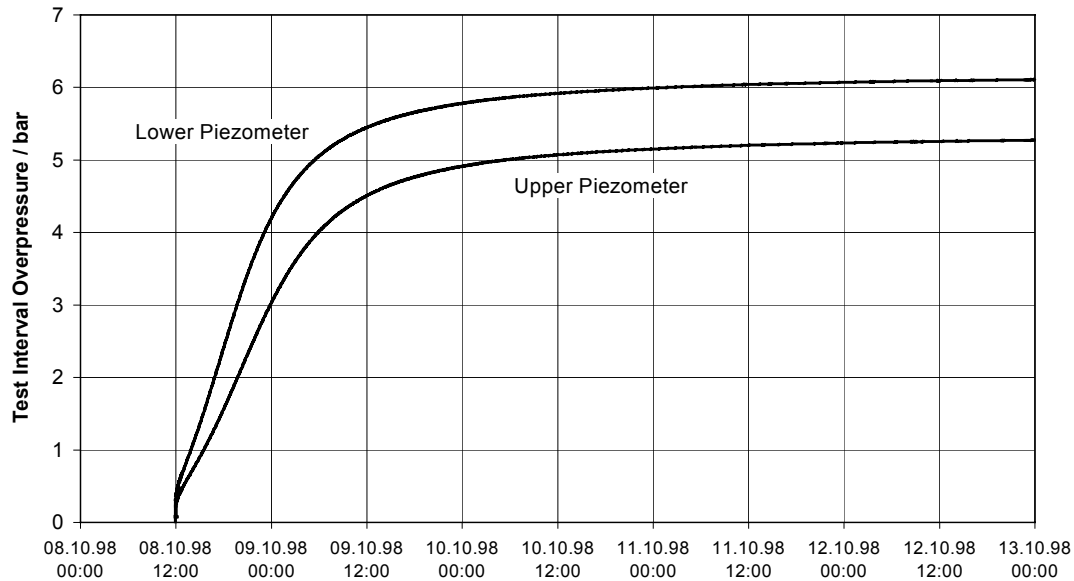
Figure 4.5   Pressure development in the piezometer probe after connection of the transducer cabinet

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

- The formation is infinite and homogeneous, and flow is strictly radial.

- The fluid pressure is 6.51 bar and 7.25 bar for the upper and lower piezometer, respectively (these are the actual measured values).

- The porosity is 0.38 (this is the mean value given by Volckaert et al. /VOL 95/.

- The borehole radius is 0.029 m (this is given by the probe dimensions).

In figure 4.6, the pressure data measured for the lower piezometer are shown together with the calculated curve for a permeability of $3 \cdot 10^{-19}$ m^2 (the best fit) and two calculated curves for $1 \cdot 10^{-19}$ m^2 and $5 \cdot 10^{-19}$ m^2 (for comparison).

A water permeability around $3 \cdot 10^{-19}$ m^2 can be regarded as rather well established. This value is also in good agreement with results of other measurements /VOL 95/.

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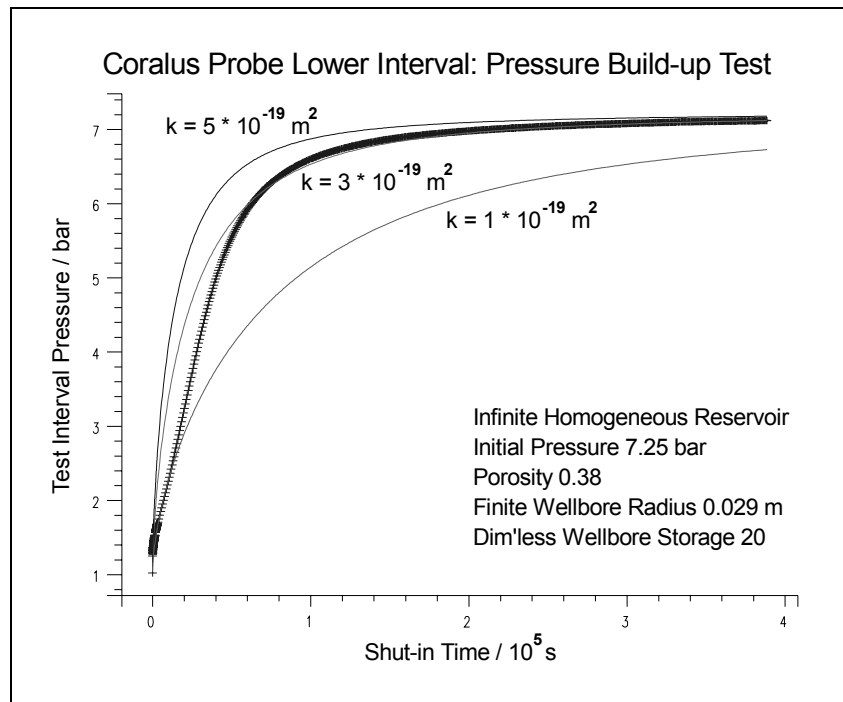
Figure 4.6 Measured (+++) and calculated (—) pressure development in the lower piezometer after connection of the transducer cabinet

The calculated pressure increase is initially somewhat steeper than the measured slope. This observation can be explained by the presence of air in the connecting tube; the computer code cannot take this into account.

The results of the evaluation for the upper piezometer agree with those shown above; the best-fit permeability was also $3 \cdot 10^{-19}$ m^2.

4.5.2 Permeability of the Boom clay formation to gas

Gas injection tests in the Boom clay probe were performed on 12th January, 1999 (prior to heating), on 13th April, 1999 (at the end of the heating phase, when the temperature at the probe had risen to about 34 °C), and on 13th October, 1999 (after cool-down). Prior to each gas injection, the piezometer was purged with nitrogen. From the pressure development during the injection and the subsequent shut-in phase, the effective permeability to gas was estimated with the use of the Weltest code /WEL 97/.

Best fits of the measured gas pressure curves were obtained with small (0.1 to 0.7) skin factors, which describe a decrease in permeability in the immediate vicinity of the probe (like a blockage of pores). The evaluated permeabilities were $3.5 \cdot 10^{-21}$ m^2 prior to heating, $3 \cdot 10^{-20}$ m^2 at the end of the heating cycle, and $8 \cdot 10^{-19}$ m^2 after cool-down. The measured and calculated pressure curves of the shut-in phase after cool-down are shown in figure 4.7 for an example.
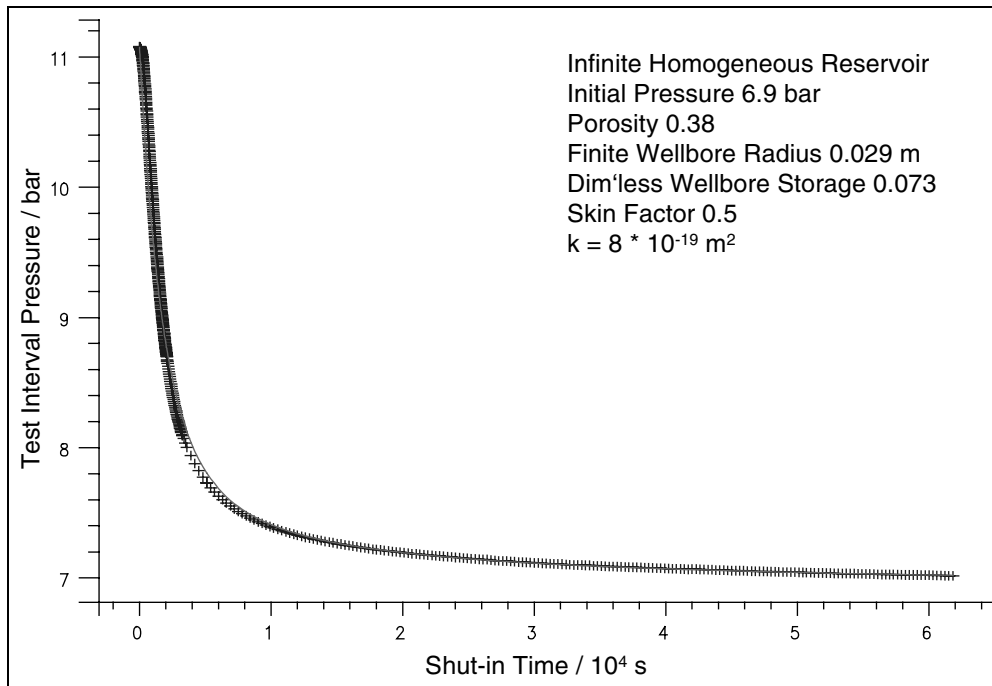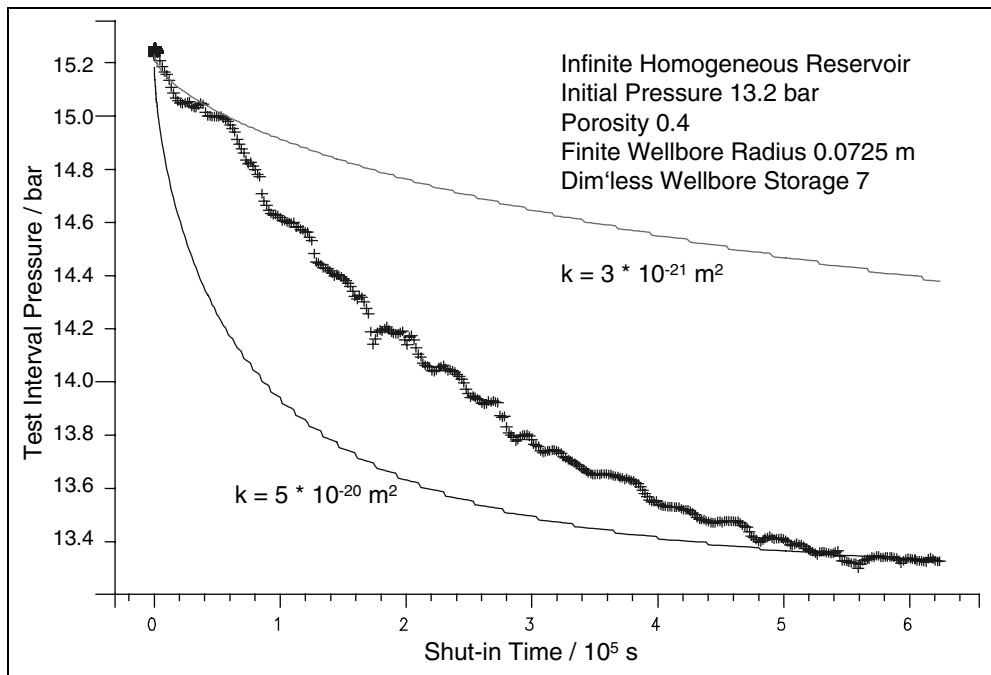

Figure 4.7   Measured (+++) and calculated (—) pressure development in the lower piezometer of the probe after the gas injection on 13th October, 1999

The gas injection tests were performed in a highly water-saturated material. Consequently, the measured effective permeabilities to gas can be expected to be extremely low in comparison with the intrinsic permeability (which is measured when only one fluid phase is present). This is obviously the case for the first two measurements. The permeability measured at the end of the heating phase is higher by one order of magnitude than that before heating; this observation is most likely due to a decrease in water saturation in the pore space, as a result either of the heating itself or of the presence of residual gas from the first injection test in the system because of the low permeability. In view of the high water saturation, the low evaluated permeabilities, and the fact that the gas had remained in the system, it is doubtful whether the model of pressure-driven Darcy flow really describes the real conditions. Other mechanisms, such as

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gas solution in the pore liquid or opening of pore space by the gas overpressure, may just as likely be the cause of the measured pressure decrease. The significance of such effects has to be estimated.

The evaluated permeability to gas after cool-down is again higher than that during heating by 1.5 orders of magnitude. It must be mentioned, however, that the CORALUS test tube had been withdrawn from the borehole in the meantime. The permeability increase is thus a consequence not only of desaturation, but also of mechanical disturbance of the clay rock. It seems that real gas flow is possible in such disturbed regions, whereas gas flow does not play a significant role in the more or less undisturbed clay before and during heating.

4.5.3 Permeability of the backfill materials to gas

Gas injection tests in the backfill were performed at the end of the heating period in each of the three backfill bodies in the lower central piezometer of the CORALUS tube. The temperature at the piezometers was about 90 °C.

For all three measurements, no satisfying fit of the measured pressure curves could be obtained. In table 4.4, lower and upper limits are therefore given for the effective permeability. The measured pressure curves lie between the two curves calculated with these permeability values, as shown in figure 4.8 for Boom clay backfill A.

Table 4.4   Effective permeability ranges for gas in the three backfill materials

	Backfill A	Backfill B	Backfill C
Material	Boom Clay	FoCa + Sand	FoCa + Glass
k_{min} / 10^{-21} m^2	3	0.5	1
k_{max} / 10^{-21} m^2	50	4	5

Possible reasons for the poor agreement between the results of the measurements and of the evaluation have already been mentioned in the previous section: Gas may be dissolved in the pore fluid, or gas pressure may progressively open or enlarge pores. The assumption of simple Darcy flow, as applied in the evaluation, is probably not valid.

Figure 4.8 Measured (+++) and calculated (—) pressure development in the lower central piezometer of backfill A after the gas injection on 13th April, 1999

4.5.4 Permeability of the backfill materials to water

An attempt was made to evaluate the pressure draw-down and subsequent recovery in the piezometers of the CORALUS tube, which resulted from sampling of the interstitial solution in the backfill, in terms of the permeability to liquid. The first sampling to be evaluated in this way had been performed on 12th December, 1998 in piezometer A1 in the Boom clay backfill. The resulting permeability value was about $3 \cdot 10^{-19}$ m^2, which agrees with the previous measurements of permeability to water in the Boom clay for-mation (see section 4.5.1). The fit is rather poor, however, since the pressure dropped below atmospheric pressure during sampling, and this situation is beyond the scope of Weltest.

At the end of the heating phase, on 28th April, 1999, another sampling series was per-formed. In piezometers A2 and C2 in the Boom clay backfill and in the FoCa clay with glass, respectively, the pressure curves were better suited for Weltest evaluation. For both tests, the evaluation yielded permeability values of about $6 \cdot 10^{-19}$ m^2. For the test at A2, the measured pressure build-up and the results of the calculation are shown in figure 4.9.
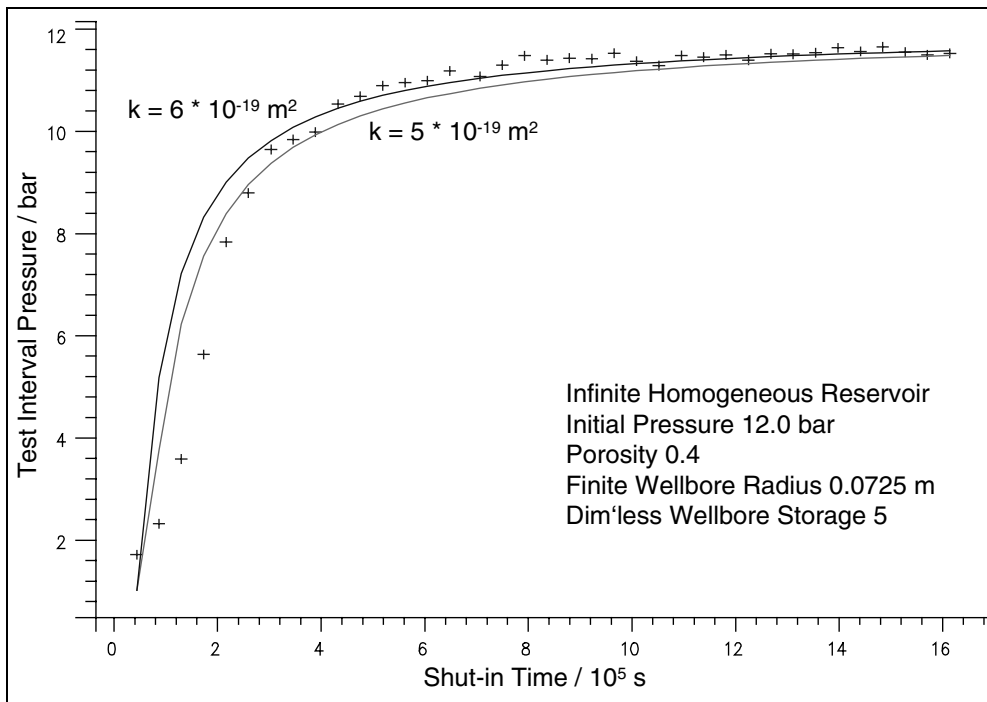
Figure 4.9   Measured (+++) and calculated (—) pressure development in piezome-
ter A2 located in the Boom clay backfill A after sampling on 28th April,
1999

Apparently, the influence of heating on the permeability of the backfill to water is very
slight. The backfill permeability is close to that of the Boom clay formation.

These evaluations have proved to be fairly successful, provided that sampling was
performed in an adequate way. Consequently, similar evaluations are also planned for
the other CORALUS tubes, in order to get more reliable data on backfill permeability.

5   Conclusions

In this report, the results of a laboratory and an in situ programme on thermal gas generation and release are presented. Petrophysical parameters such as diffusivity, permeability, porosity, and internal surface were thereby determined for different backfill materials. The period of investigation extended from 1996 to 2000. The following backfill materials were considered:

- dried Boom clay (backfill A)

- 60 per cent FoCa clay with 35 per cent sand and 5 per cent graphite (backfill B) (mass contents)

- 95 per cent FoCa clay with 5 per cent glass powder (backfill C) (mass contents)

In situ measurements were performed on the inactive test tube 1 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 will be performed from 2000 to 2004, is 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).

Within the scope of the laboratory programme, the gas release from the backfill materials was determined at different temperatures (40 and 90 °C), in different contact atmospheres (inert and aerobic), and with different water contents (natural dry stage and additional water).

The only gas which was released in significant amounts is carbon dioxide. At a temperature of 90 °C, up to 559 l per 1000 kg was detected in the Boom clay samples, and up to 159 l per 1000 kg in the FoCa clay samples. The influence of temperature on the generation and release of this component is significant, but the effect of the atmosphere is not. In the dry version with air in the residual volume, the carbon dioxide release is comparatively low (up to 73 l per 1000 kg). This component is evidently adsorbed on the internal surface of the clay. In the wet stage, water is already adsorbed

on the internal surface of the clay. Therefore, this component is desorbed and released. If the temperature is increased from 40 to 90 °C, the amount of released carbon dioxide increases by a factor of 10 to 20. Further investigations on the origin of the carbon dioxide are necessary, since it might be generated by oxidation of organic components or by decomposition of calcite. Both components are present within the clay.

The generation of hydrogen and methane is comparatively slight and therefore less important.

In the course of the current programme, the different backfill materials were exposed to temperatures of 40 and 90 °C for 100 days. Further investigations are necessary to determine whether this time is sufficient for the entire gas generation process. Up to 559 l of carbon dioxide is generated per 1000 kg of backfill material; this may already suffice for pressurising the gas-tight sealed boreholes. It may therefore be necessary to take this into account in conjunction with the long-term safety concept.

The diffusivities of the different gases at room temperature (20 °C) in the air-dry stage of the backfill materials are in the range from $100 \cdot 10^{-9}$ to $400 \cdot 10^{-9}$ m^2/s. No significant differences were observed between the different backfill materials and the different gas components. In the air-dry stage of the backfill materials, the diffusivity does not seem to be influenced by the temperature. Variations are within the limits of error.

In the flooded stage of the backfill material, the diffusivity of the gases hydrogen, helium, methane, neon, argon, and krypton at 20 and 40 °C is below the detection limit of $0.1 \cdot 10^{-9}$ m^2/s. Carbon dioxide is the only component with a diffusivity above the detection limit; the value is in the range from 0.1 to $0.6 \cdot 10^{-9}$ m^2/s. The reason for this difference is the higher solubility of carbon dioxide in water at 20 °C, that is, 0.087 litre per kg of water, in comparison with a range between 0.003 and 0.018 litre per kg of water for the solubility of the other gases.

The diffusivities at 90 °C in the flooded stage of all three backfill materials are in the range from $0.1 \cdot 10^{-9}$ to $4 \cdot 10^{-9}$ m^2/s. The reason for the higher diffusivities may be the fact that at 90 °C the pore volumes of the samples are filled not only with water in the liquid phase, but also with water in the vapour phase. Consequently, diffusion takes place preferentially in the gas-filled pore volume, rather than in the water-filled pore volume.

With values in the range of 10^{-13} m^2, the permeability of the different backfill materials to gas (nitrogen) in the air-dry stage is comparatively high and does not vary significantly. The backfill materials in the air-dry stage represent an open system in which gases can diffuse and migrate without significant resistance. Measurements of gas permeability in the flooded stage, which were performed up to a gas injection pressure of 0.9 MPa (9 bar), have not indicated any gas flow within a period of 24 hours. This means that the backfill materials are gas-tight up to 0.9 MPa.

The porosity of the compacted samples in the air-dry stage, which is relevant for gas permeability and gas diffusion in that stage, is in the range between 11.9 and 26.7 per cent. There are no significant differences among the three backfill materials. This corresponds with the fact that gas diffusivity and gas permeability do not differ significantly among the backfill materials.

The total porosity of the absolute dry (gas-filled pore volume) or flooded (water-filled pore volume) compacted samples is in the range between 26.0 and 45.3 per cent, with no significant differences among the three backfill materials. This porosity and its distribution are important for the gas break-through pressure and two-phase flow in the partly saturated stage of the backfill material.

The internal surface areas of the uncompacted backfill materials are:

dried Boom clay (backfill A)	20.8 to 21.8 m^2/g
FoCa clay with sand and graphite (backfill B)	9.5 to 10.0 m^2/g
FoCa clay with glass powder (backfill C)	12.1 to 12.6 m^2/g

Since the internal surface is important for the sorption and migration of corrosion products and released radionuclides, measurements should also be performed on the compacted backfill materials.

For the purpose of in situ measurements on gas generation and release, samples of the formation water which had been injected into the different backfill materials of test tube 1 were extracted and analysed prior to and during heating. The only gases which could be detected were oxygen, carbon dioxide, and methane. Hydrogen was not found above the detection limit. The injected water was already saturated with oxygen

(362 to 560 l / 1000 kg). During the test, the content of oxygen decreased, and carbon dioxide was generated up to 398 l / 1000 kg. Prior to and during heating, the gas content in the formation water of the different backfill materials did not vary significantly. The time periods until water sampling of 21 days prior to heating and 46 days during the heating phase were obviously too short for reaching steady-state conditions with respect to the physico-chemical parameters, as well as the equilibrium of the dissolved gases. The test on the inactive tube 1 indicated that the methods of sampling and analysis yield acceptable results and can be applied to the active tubes 2, 3, and 4. However, a much longer time allowance is essential for reaching equilibrium in the different stages.

The measurements of permeability to gas resulted in extremely low values both for the Boom clay formation and for the different backfill bodies. This is not surprising, in view of the fact that the media were highly water-saturated. Heating did not significantly affect the permeability. A significant increase of gas permeability in the Boom clay was detected only after withdrawal of the CORALUS test tube. However, this is probably due to mechanical damage to the formation. In summary, gas flow in the water-saturated clay seems probable only in disturbed zones close to an opening.

The permeability to liquid was determined to be about $3 \cdot 10^{-19}$ m^2 for the Boom clay and in the range of $6 \cdot 10^{-19}$ m^2 for the backfill. The value for the Boom clay is in good agreement with earlier measurements. Future measurements in the backfill will provide more data.

On the whole, the laboratory and in situ investigations in the CORALUS 1 project have indicated that the equipment and the methods are adequate for use in the CORALUS 2 project.

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