

International
Progress Report

IPR-06-05

Äspö Hard Rock Laboratory

LTDE Long-Term Diffusion Experiment

Functionality tests with short-lived radionuclides 2005

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January 2006

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Report no.
IPR-06-05

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No.
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Date
January 2006

Date
2007-08-15
Date
2007-09-27

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Keywords: Crystalline rock, Fractured rock, Transport properties, Diffusion, Sorption, Diffusivity, In-situ measurements, Radionuclides, Tracers

This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

Abstract

Within the frame of the LTDE project (*in situ* studying of diffusion and sorption processes over longer time-scales) a functionality test with short-lived radionuclides has been performed. This report describes the performance and procedures of the functionality test together with the obtained results.

The main objectives of the test were to test injection and sampling procedures as well as to check the functionality of individual systems such as, for example, circulation equipment, pressure regulator, sensors, on-line measurements and alarms. It could be concluded from the functionality test that all systems worked overall as expected. Some minor adjustments and modifications are proposed to increase the functionality prior to a future long term test. Also, the injection and sampling procedures concerning the tracers functioned as planned.

Another objective of the test was to investigate if sorption, in terms of decreasing tracer concentration in the test section, could be monitored. Both non-sorbing and sorbing tracers were used. The following trend could be observed: $\text{Ca(II)} \leq \text{I(-I)} < \text{Np(V)} < \text{Cd(II)} < \text{Cs(I)} < \text{Lu(III)} < \text{Hf(IV)}$, where no sorption of Ca(II) is observed and I(-I) shows a weak sorption. The sorption results are discussed in relation to speciation calculations for the different species. Surface sorption coefficients and matrix sorption coefficients are evaluated for a batch sorption and a sorption-diffusion model respectively. However, the sorption data presented in this report should be regarded as indicative rather than absolute. Further, the results from the tracer experiment indicate that sufficient mixing of the tracer solution(s) in the test section will be obtained for a long term diffusion experiment as planned. Short-time experiments with duration of hours to days are however unsuitable with the present borehole configuration.

The duration of the functionality test was four weeks. pH and redox potentials were continuously monitored with an electrochemical flow cell developed for measurements at high pressures. Furthermore, continuous pressure monitoring and additional sampling and analysis for tracers in the first guard section, particles, microbes, radon, sorption of tracers on tubing and groundwater chemical composition was done. The results are shown and discussed in the report.

Sammanfattning

Inom ramen för LTDE projektet (*in situ* studier av diffusions- och sorptionsprocesser) har funktionalitetsprovning med kortlivade radionuklider genomförts. Rapporten beskriver utförande och resultat för funktionalitetstesterna.

De huvudsakliga syftena med provningen var att prova injicerings- och provtagningsprocedurer samt att undersöka funktionaliteten för enskilda system såsom cirkulationsutrustning, tryckregulator, olika givare, on-line mätningar och larmfunktioner. Generellt sett fungerade alla system som förväntat. Några mindre justeringar och förändringar föreslås för att förbättra vissa funktioner före ett framtida långtidsförsök. Även injicering och provtagningsprocedurer fungerade som planerat.

Ett annat syfte med provningen var att undersöka om sorption, i form av minskande spårämneskoncentration i testsektionen, kunde mätas med utrustningen. Både icke-sorberande och sorberande spårämnen användes. Följande trend i sorptionsstyrka observerades: $\text{Ca(II)} \leq \text{I(-I)} < \text{Np(V)} < \text{Cd(II)} < \text{Cs(I)} < \text{Lu(III)} < \text{Hf(IV)}$, där ingen sorption av Ca(II) observerades och jod sorberade svagt. Sorptionsresultaten diskuteras i relation till specieringsberäkningar för respektive grundämne. Ytsorptions- och matrissorptionskoefficienter utvärderades för en enkel ytsorptionsmodell samt en endimensionell sorptions- diffusionsmodell. Sorptionsresultaten skall dock ses som indikativa och inte absoluta värden. Resultaten indikerar att tillräcklig omblandning av injicerade spårämneslösningar i testsektionen fås för ett kommande långtidsförsök. Snabba experiment med en varaktighet av timmar till dagar är dock olämpliga att genomföra vid LTDE med nuvarande borrhålskonfigurering pga. tiden att nå fullständig omblandning.

Funktionalitetstesten varade i 4 veckor. pH och redox-potentialer mättes kontinuerligt med en elektrokemisk flödescell som utvecklats för mätningar vid höga tryck. Vidare så utfördes kontinuerlig tryckmonitoring och provtagning och analys av spårämnen i grundvattnet, partiklar, mikrober, radon, sorption av spårämnen på slangar samt kemisk analys av grundvattnet. Resultaten visas och diskuteras i rapporten.

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1 Introduction

1.1 Background

Transport of radionuclides in rock fractures is presently studied within the TRUE experimental programme. To be able to study diffusion and sorption processes over longer time-scales a long term diffusion experiment, LTDE, has been set up at Äspö Hard Rock Laboratory in Sweden. The original experimental plan was laid out by Byegård et al., 1999. Since then the experimental concept has been modified to some extent, and is currently being revised again. A recent review by Peter Vilks, AECL Canada, gives a good overview of the developments and the present status of the project (Vilks, 2004). The main objectives of LTDE are:

- To investigate the magnitude and extent of diffusion in matrix rock from a natural fracture and in fresh, un-altered rock *in situ* under natural rock stress conditions and hydraulic pressure and groundwater chemical conditions.
- To obtain data on sorption properties and processes of individual radionuclides on natural fracture surfaces and internal surfaces in the matrix.
- To compare laboratory derived diffusion constants and sorption coefficients for the investigated rock fracture system with the sorption behavior observed *in situ* at natural conditions, and to determine if laboratory scale sorption results are representative also for larger scales.

The LTDE site is located in the niche at tunnel section 3065 m at a depth of approximately -410 masl. KA3065A03 is the experimental borehole and KA3065A02 has served as exploration pilot borehole to find a suitable target structure on which to perform the experiment, see Figure 1 for borehole locations.

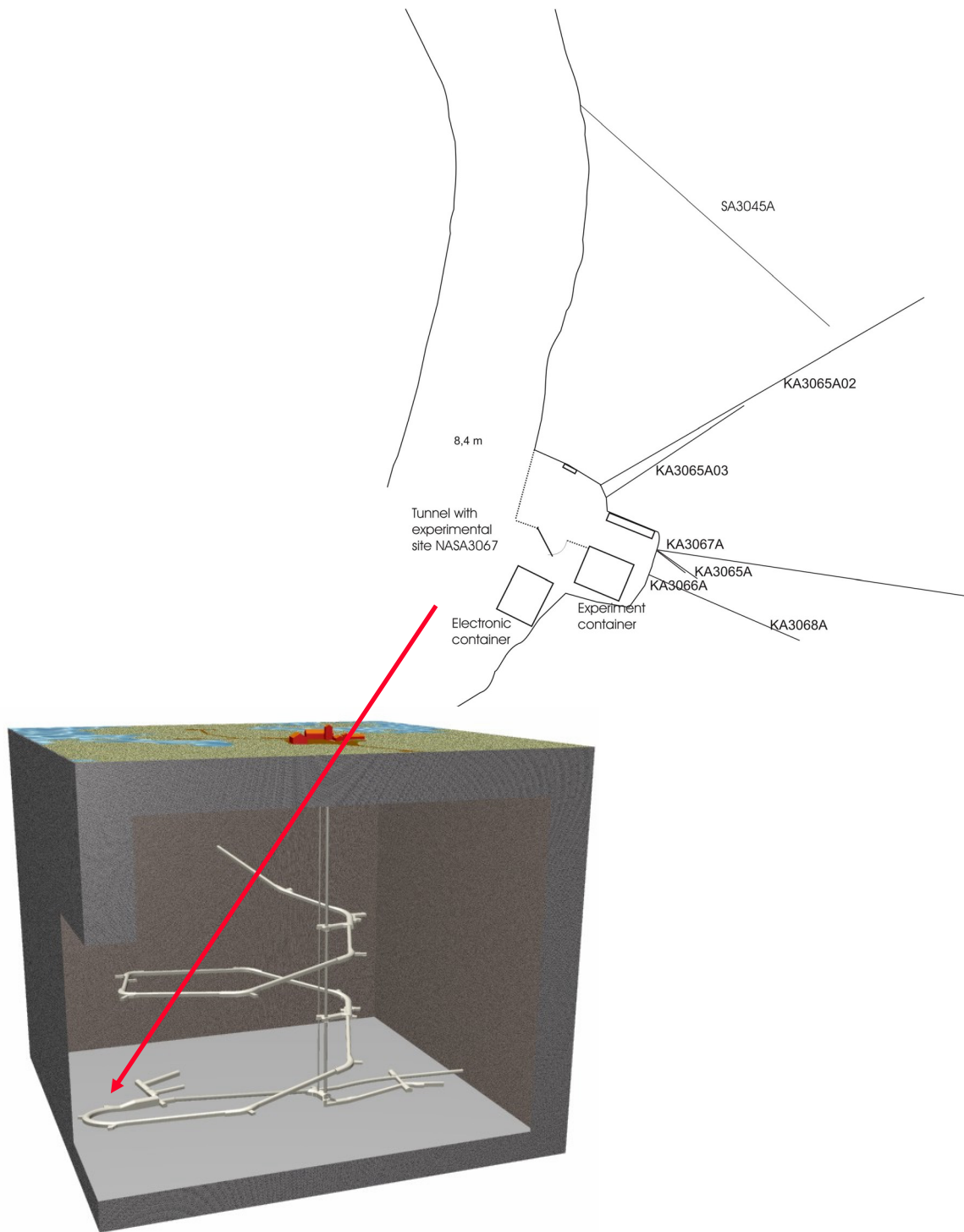


Figure 1. Location of the LTDE experimental hole KA3065A03, and the pilot hole KA3065A02 used to help characterize the rock in the vicinity of KA3065A03.

In the earlier versions of test design only the stub itself was planned to be used for the matrix diffusion study. However, to be able to study also the diffusion in non-decompressed rock, without open fractures, a small diameter (36 mm) borehole, approximately one metre long, has been drilled in the centre of the stub.

At the end of the experiment, the rock volume subject to diffusion is planned to be over-cored, sectioned and analysed for tracer activity/concentration. The in situ experimentation is supported by various types of mineralogical, geochemical and petrophysical analyses.

Winberg et al. (2003) have described the geologic and geotechnical features of the rock matrix in the vicinity of the test area in detail. Borehole imaging by BIPS (Borehole Image Processing System) and core logging in the two boreholes were used to correlate fractures in the two holes. The correlation was substantiated by mineralogy and geochemical studies including stable isotopes.

Within the framework of collaboration between SKB and Ontario Power Generation's (OPG) Nuclear Waste Management Division supporting laboratory experiments on core samples from the LTDE borehole KA3065A03 are in progress at Atomic Energy of Canada Limited, AECL (Vilks et al., 2005). The experimental programme consists of porosity measurements, diffusion cell experiments, radial diffusion experiments and permeability measurements.

During 2004 pre-tests including hydraulic testing (flow logging, interference and pressure build-up tests) and non radioactive tracer tests (dilution test and leakage testing) have been performed (Wass, 2005)

Installation and installation tests of the experimental set up at LTDE have been finalised during 2005 (according to the SKB internal document AP TD F79-01-49 v.3). A schematic diagram of the experimental system for monitoring and sampling solutions from the test section and the inner guard section is given in Figure 2.

This report describes a functionality test with short lived radionuclides that was performed during September to October 2005 according to AP TD F79-05-003 (SKB internal document). This test is a final preparation for forthcoming tests with more long-lived radionuclides at the LTDE site.

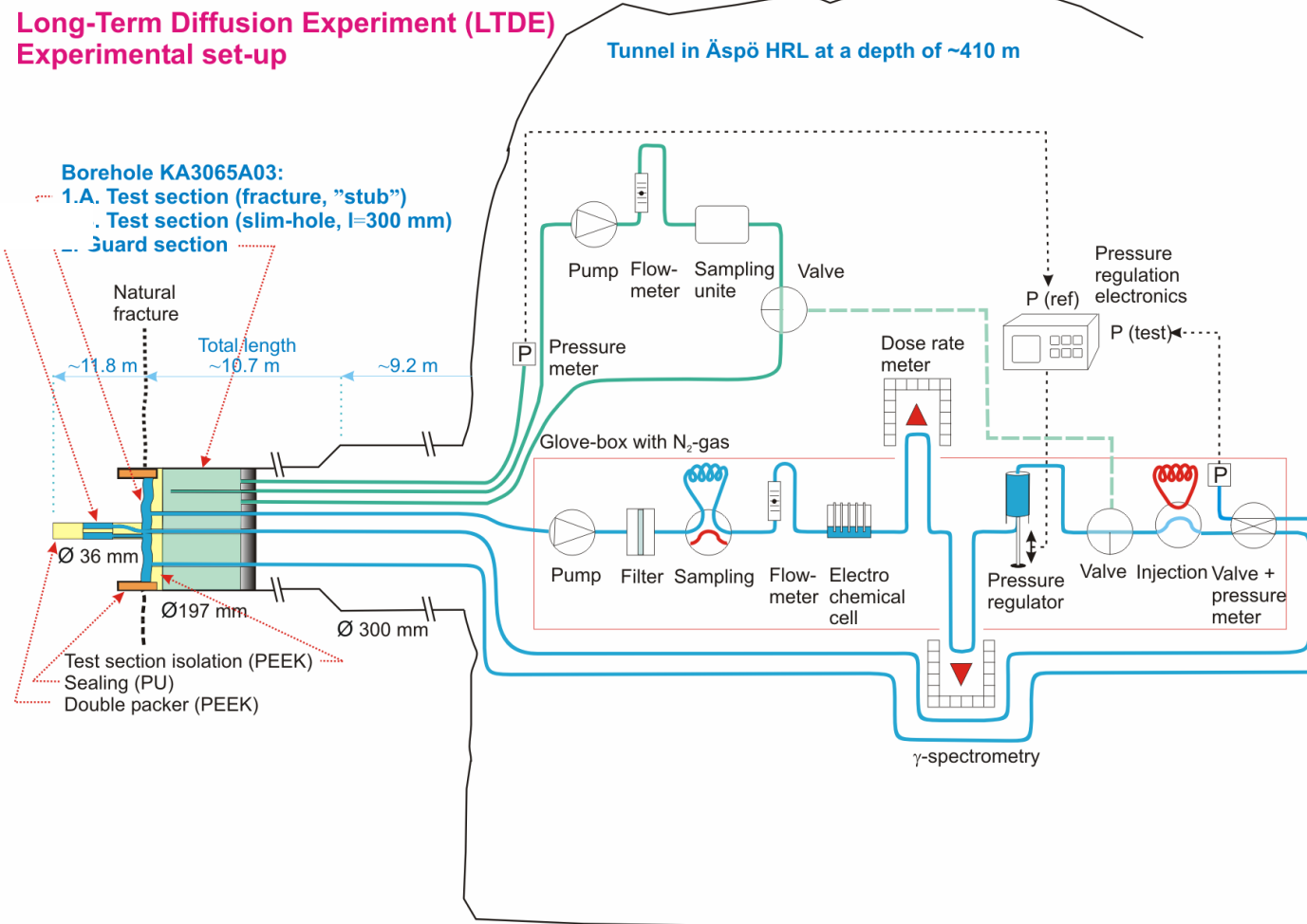


Figure 2. Schematic diagram of experimental system for monitoring and sampling solutions from the test section and the inner guard section. The total lengths given are measured from the borehole casing. An on-line measurement of gamma-radiation is installed in the guard section circulation but not shown in the figure.

1.2 Objectives

Before the start of the long term experiment a functionality test with short lived radionuclides was performed during September to October 2005. The results are presented in this report. The objectives of the tests were mainly to:

- Test the complete experimental set up with respect to functionality and safety, including:
 - Individual functions of circulation equipment, pressure regulator, sensors, monitoring systems, alarms, remote access to computers, backup of data etc.
 - Functions and equipment at Baslab, (the radiochemistry lab).
 - The transport of samples between Baslab and the LTDE site.
 - Radiation protection services and needs.
- Develop and test the sampling and injection procedures in the test section and to check that appropriate mixing of the injected tracer solutions can be obtained.
- Investigate if sorption processes on the stub surface can be monitored with the present experimental set-up, i.e. measurement of the decrease of tracer concentration in the test section volume.

2 Performance

2.1 Equipment

2.1.1 Borehole KA3065A03

The experimental set-up consists of a telescoped large-diameter borehole (KA3065A03) that intercepts a previously identified fracture. The intersected part of the fracture is packed off using a special "packer" which seals around the developed core stub. A solution with conservative and sorbing radioactive tracers can be injected and circulated in the isolated section. A small diameter (36 mm) borehole, approximately one metre long, has been drilled in the centre of the stub. 300 mm section of the small diameter borehole is packed off for tracer circulation purposes. Further, the borehole outside the stub is packed off with mechanical and inflatable packers to avoid effects of the acting hydraulic gradient. A schematic diagram of the packer system used to complete the LTDE test hole is shown in Figure 3.

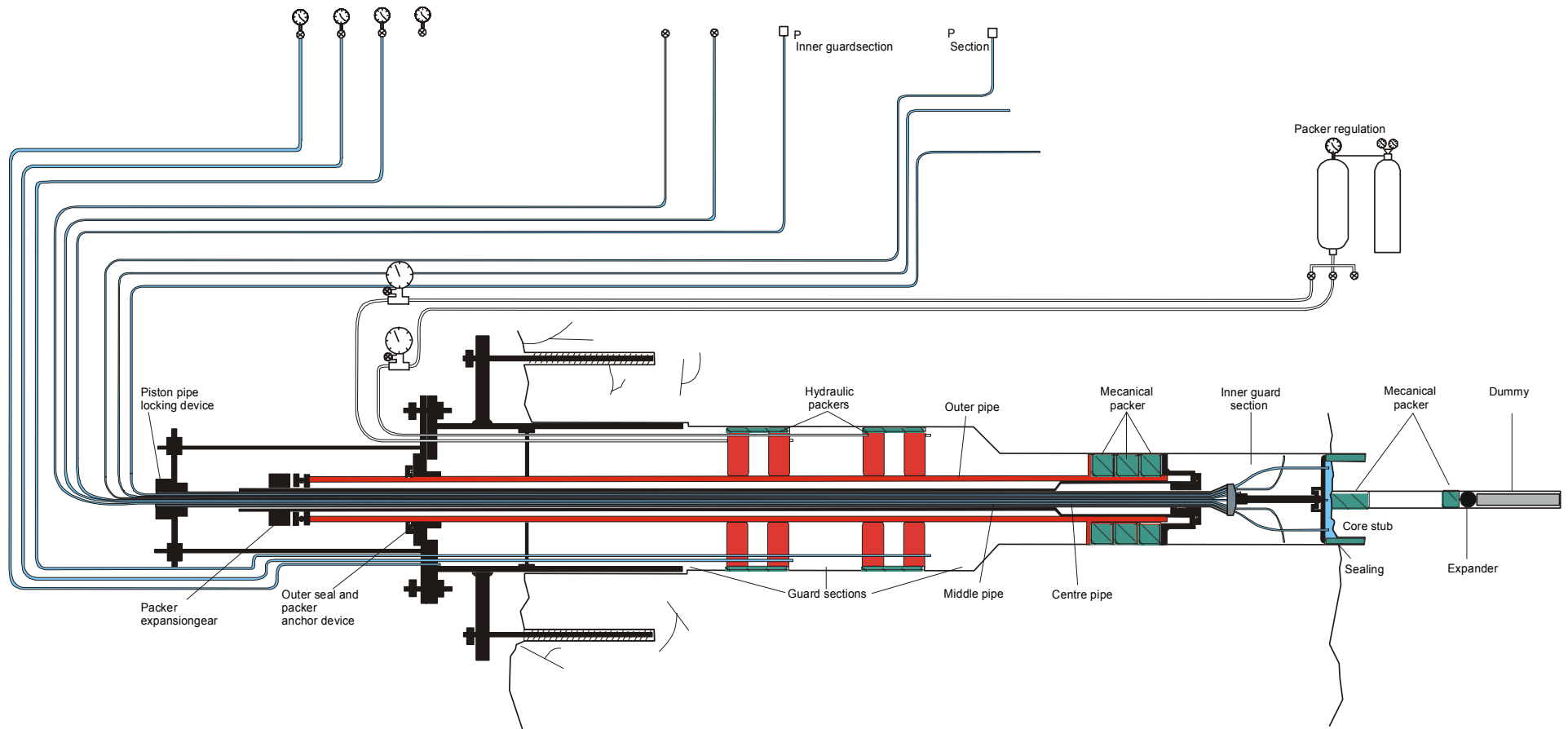


Figure 3. Schematic diagram of the packer system used to complete the LTDE borehole installation (KA3065A03+slimhole).

2.1.2 Circulation equipment in KA3065A03:1

All circulation equipment such as pump, flow meter and on-line measurement of radioactivity and electrochemical flow cell are placed in inert gas boxes. The boxes are flushed with nitrogen in order to reduce the oxygen content in the test section groundwater. A schematic diagram of the circulation set-up is shown in Figure 4. Pictures of the inert gas boxes are shown in Figures 5 and 6.

All equipment is attached to 6-port valves in PEEK (Upchurch Scientific, Injection Valve V-540) as shown in Figure 4. The flow can be directed through the external unit attached to ports 1 and 4, or it can be bypassed to the next valve according to Figure 4. When the valve is in the bypass position, the external units can be flushed using water from the first guard section. The flushing is done through ports 2 and 3 in order to fill up and pressurise the unit with groundwater prior to connecting it to the circulation.

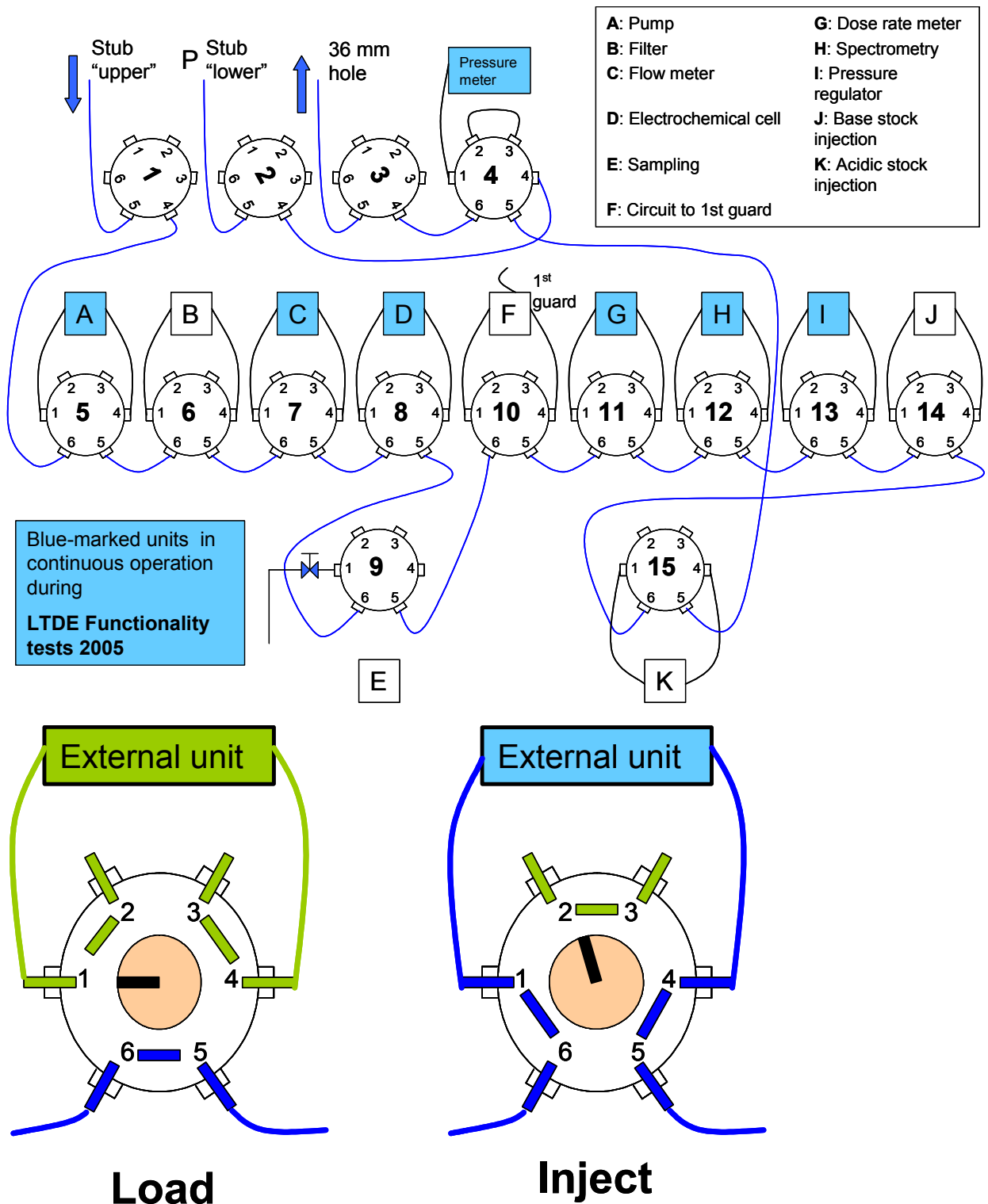


Figure 4. Schematic diagram of the circulation set-up during the tests (top) and connection diagram of the 6-port valves used for connections of equipment to the circulation line (bottom).



Figure 5. Inert gas glove box for all circulation equipment excluding the pressure regulator which is contained within a separate inert gas box.



Figure 6. Inert gas box for the pressure regulator piston. The pressure regulators consists of a step motor (lower picture) which operates a piston in a PEEK mantled cylinder (upper picture). The motor is controlled by a separate electronic unit. The desired difference pressure between the test section (KA3065A03:1) and the reference section (first guard section KA3065A03:2) is set in the control unit.

2.1.3 On-line monitoring equipment in KA3065A03:1

γ -spectrometry

The radioactivity concentration in the test section groundwater is measured on-line by an HPGe-detector (ORTEC, relative efficiency 12%). The detector is electrically cooled (XCooler, ORTEC). A digital multi channel analyser (DigiDart, ORTEC) is connected to the LTDE1 computer through an USB interface. In order to avoid ground loop disturbances, a fibre optic converter (OPTICIS optical USB extension cable M2-100) is placed between the DigiDart and the computer to create a galvanic isolation of the two units. The spectra were collected and analysed using the software GammaVision 5.31 (ORTEC).

The circulation tubing passes in front of the detector through a loop. The loop is arranged so that the volume of the tubes exposed to the detector is about 5 ml. The distance between the detector window and the tube was approximately 1, 5 cm. A picture of the lead shield and parts of the detector is shown in Figure 7.



Figure 7. Lead shield and parts of the HPGe-detector used for on-line radioactivity concentration measurements.

Test section effective dose rate

The effective dose rate in a separate loop of the test section (~35 ml volume) was monitored using a GM-probe connected to a RNI-instrument (RNI AB) in a separate lead shield. The RNI-instrument has a data connection to the LTDE1-computer through a RS-232 interface. The software RNICom is used to collect and display data from the instrument. This monitoring is used to give alarm if a sudden decrease in the dose rate of the test section loop should occur as a result of a leakage in the test section. A picture of the lead shield and the back part of the probe is shown in Figure 8.



Figure 8. Lead shield and back part of the GM-probe used for on-line dose rate monitoring.

Electrochemical flow cell

A flow-cell and a measurement system have been developed for continuous measurements of pH and Eh at high pressures (SKB internal document, AP TD F63-03-45). Figure 9 shows the flow-cell, which is made entirely in PEEK. The electrodes situated in the flow-cell are two glass electrodes, a platinum electrode (Pt), a gold electrode (Au) and a reference electrode (Ag, AgCl). The pH and reference electrodes are specially designed for measurements under high pressure (Pehkonen, 2005a and b). Calibrations are performed by circulation of calibration solutions (pH 4+quinhydrone, pH 7+quinhydrone and pH 10). Calculation of calibration constants and recalculation of measurement data given in mV is done manually.

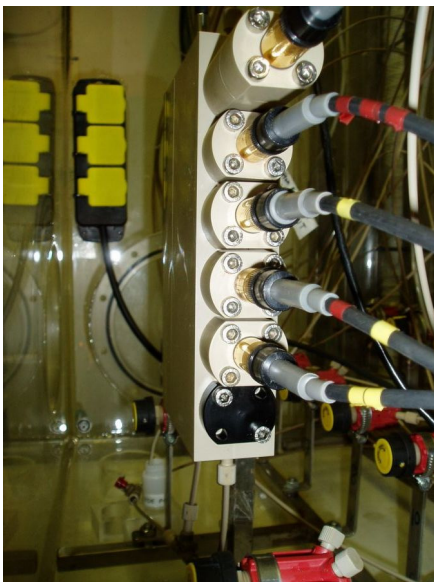


Figure 9. Electrochemical flow cell used for on-line measurements of pH and Eh.

2.1.4 Other equipment

Effective dose rate at fence and in container 1

The effective dose rate (in units of $\mu\text{Sv/h}$) at the fence towards the tunnel and in container 1 was monitored using RNI 10/SR-instruments (RNI AB). The data were collected through a computer interface in the same way as described for the test section dose rate monitoring above.

Monitoring of radioactivity in the first guard section (KA3065A03:2)

The first guard section KA3065A03:2 have a circulation equipment placed in a cabinet outside of container 1. The radioactivity in the groundwater of the first guard section was monitored by a 1 inch plastic scintillator probe connected to a RNI-instrument. The probe was placed within a loop of the guard tubing in a separate lead shield. The volume of the loop is approximately 85 ml.

Other equipment

Leak indicators are placed inside the inert gas boxes, on the floors of the containers and in the cabinet for the guard and pilot hole circulations equipment. Difference pressure transmitters are monitoring the pressure in the inert gas boxes. Three network cameras are used for remote observations of container 1 and the borehole. Temperature sensors are monitoring the temperature at a number of different positions on the site. Pressure monitors from all borehole sections and surrounding boreholes are located in a separate cabinet. All monitoring equipment is connected to the InTouch monitoring and control software in the computer LTDE2 through a PLC interface in Container 2. Groups of transmitters in InTouch are connected to the alarm system Alpha at Äspö HRL, which in turn is connected to Clab (Central interim storage facility for spent nuclear fuel, located near the Oskarshamn Nuclear Power Plant OKG) control room for 24h monitoring.

2.2 Tracers

Both sorbing and non-sorbing tracers were used in the experiment. The radionuclides that were used are summarised in Table 1. The use of the different radionuclides aims at studying different retardation processes, e.g. sorption and diffusion. The radionuclides have been categorised in two groups after their primary usage:

- A. Non-sorbing tracers, i.e. tracers that are assumed to diffuse without retardation due to sorption onto mineral surfaces. The inorganic anions Br^- and Cl^- belong to this group.
- B. Sorbing tracers, i.e. tracers that are retarded by adsorption onto mineral surfaces. These tracers are aimed to estimate the impact of sorption on the penetration into the rock. The proposed tracers can be divided into three different subcategories within this group:
 1. Tracers for which the sorption is dominated by a cation exchange mechanism
 2. Tracers for which the sorption is dominated by a surface complexation mechanism

3. Tracers that are dependent of an electrochemical reduction in order to reach the tetravalent state (oxidation state IV) which is considered to be very strongly sorbing. The corresponding higher oxidation state for the respective tracer is thus considered to be weaker sorbing

Consequently, the sorbing tracers are divided into the subcategories B1, B2 and B3.

Table 1. Summary of radionuclides used in the experiment. Radionuclides given in italic style are by-products or daughters in the production of the radionuclides aimed for primary use in the experiment (i.e. the radionuclides in non-italic style). By-products in radiotoxicity class B and C with a total radioactivity below 1 kBq have been omitted.

Isotope	$t_{1/2}$	Decay mode	Oxidation state	Group	Radio-toxicity class	Injected activity (kBq)
^{24}Na	14.96 h	β^-, γ	Na(I)	B1	C	10
^{47}Ca	4.54 d	β^-, γ	Ca(II)	B1	C	97
^{47}Sc	3.35 d	β, γ	Sc(III)		C	9.0 ¹⁾
^{45}Ca	163 d	β, γ	Ca(II)		B	4.3 ²⁾
^{64}Cu	12.7 h	β^-, β^+	Cu(II)	B2	C	6.0 ¹⁾
^{115}Cd	2.22 d	β^-, γ	Cd(II)	B2	C	193
^{115}Cd	44.8 d	β, γ	Cd(II)		C	7 ¹⁾
^{131}I	8.02 d	β^-, γ	I(-I)	A	B	95
^{131}Cs	9.69 d	ϵ, γ	Cs(I)	B1	C	3.6E4 ³⁾
^{131}Ba	11.5 d	ϵ, γ	Ba(II)		C	1.5
^{177}Lu	6.71 d	β^-, γ	Lu(III)	B2	C	1.7E3
^{181}Hf	42.39 d	β^-, γ	Hf(IV)	B2	C	14
^{175}Hf	70.0 d	ϵ, γ	Hf(IV)		C	1.9
^{239}Np	2.355 d	β^-, γ	Np(V), Np(IV)	B3	C	890
^{239}Pu	2.4E4 y	α	Pu (?)		A	2.4E-4
^{140}Ba	12.75 d	β, γ	Ba(II)		B	2.5
Sum (Radiotoxicity classed)						23 060 A: 2.4E-4 ⁴⁾ B: 102 C: 3.9E4

- 1) The non-injected part of the stock solution had an activity below the minimum detectable concentration at the time of measurement. Instead the non-injected part is calculated based on the average of the radionuclides that could be measured with enough accuracy.
- 2) Calculated value based on neutron absorption cross section and the isotope enrichment of ^{44}Ca in the Ca-target.
- 3) No calibration source available. Total amount estimated from irradiation calculations.
- 4) Calculated value based on neutron absorption cross sections for ^{238}U .

2.3 Performance of functionality test with radioactive tracers

One of the objectives of the functionality test with short-lived radionuclides were to test injection and sampling procedures and the functionality of the entire system i.e. circulation equipment, on-line measurement with HPGe-detector and environmental monitoring. The performance of the test with radioactive short-lived tracers is described below. Standard procedures for preparation of stock solutions and calibration of detectors are not discussed in detail.

2.3.1 Preparation of stock solutions

Stock solutions comprising the short-lived tracers were prepared at Baslab (Clab, SKB). Two neutron-irradiated quartz glass ampoules had been prepared with adequate amounts of targets (salts) and sent in advance to the Institute for Energy Technology (IFE) Kjeller, Norway. The irradiated ampoules delivered from IFE were:

1. Irradiated salts for production of ^{24}Na , ^{47}Ca , ^{64}Cu , ^{82}Br , ^{115}Cd , ^{131}I , $^{135\text{m}}\text{Ba}$ (BaCO_3 isotope enriched in ^{134}Ba was planned to be used), ^{177}Lu , ^{181}Hf and ^{239}Np (this solution was injected first)
2. Irradiated BaCO_3 of natural isotope composition for production of ^{131}Cs (second solution injected)

Solution 1

The contents of the ampoule was dissolved in an acidic aqueous solution and moderately heated while stirred. After cooling, the solution was checked for its radioactivity content, filtered and transferred to a glass bottle. Next, the solution was pH-adjusted. To avoid sorption phenomena on glass vessels and tube walls for sorbing tracers, the solution was prepared in a weak acid solution of approximately pH 1.5. A small amount of a separate stock solution comprising ^{131}I was transferred to a cation exchange resin and eluted with distilled water. After control measurement an appropriate amount of the ^{131}I solution was transferred to solution 1. The solution was then sampled to determine the final radioactivity content.

Solution 2

The preparation of the ^{131}Cs stock solution is described in Appendix A. The stock solution was filtered (0.45 μm) and transferred to a glass vessel. As the amount of acid injected in solution 1 may exceed the buffer capacity of the test section site it had to be neutralized with a base, NaOH, which was added to solution 2 (~pH 12.5). The solution was then sampled to determine the final radioactivity content.

The two ready mixed stock solutions were then checked for external contamination, cleared and transported as a radioactive transport to the LTDE test site according to the routines at OKG.

2.3.2 Injections

Principle for injection

The first injection (solution 1) was done in acidic solution in order to avoid precipitation of some tracers (mainly Hf and Lu) and to minimise sorption on equipment before the tracers reached the test section. The second injection (solution 2) contained an excess of base in order to neutralise the acidic first injection.

The principle for the injection was to inject the tracers as pulses with a plug flow and short but sufficient time spacing between the two injections. The acidic pulse would thus reach the test section a short time before the basic pulse and the water would be pH-equilibrated to a large extent by the mixing in the first passage of the pulses through the slimhole and stub sections. If precipitation or strong sorption would occur immediately following neutralisation, this procedure would at least make it occur mainly within the slimhole or stub sections. A schematic picture of the serial pulse injections is shown in Figure 10.

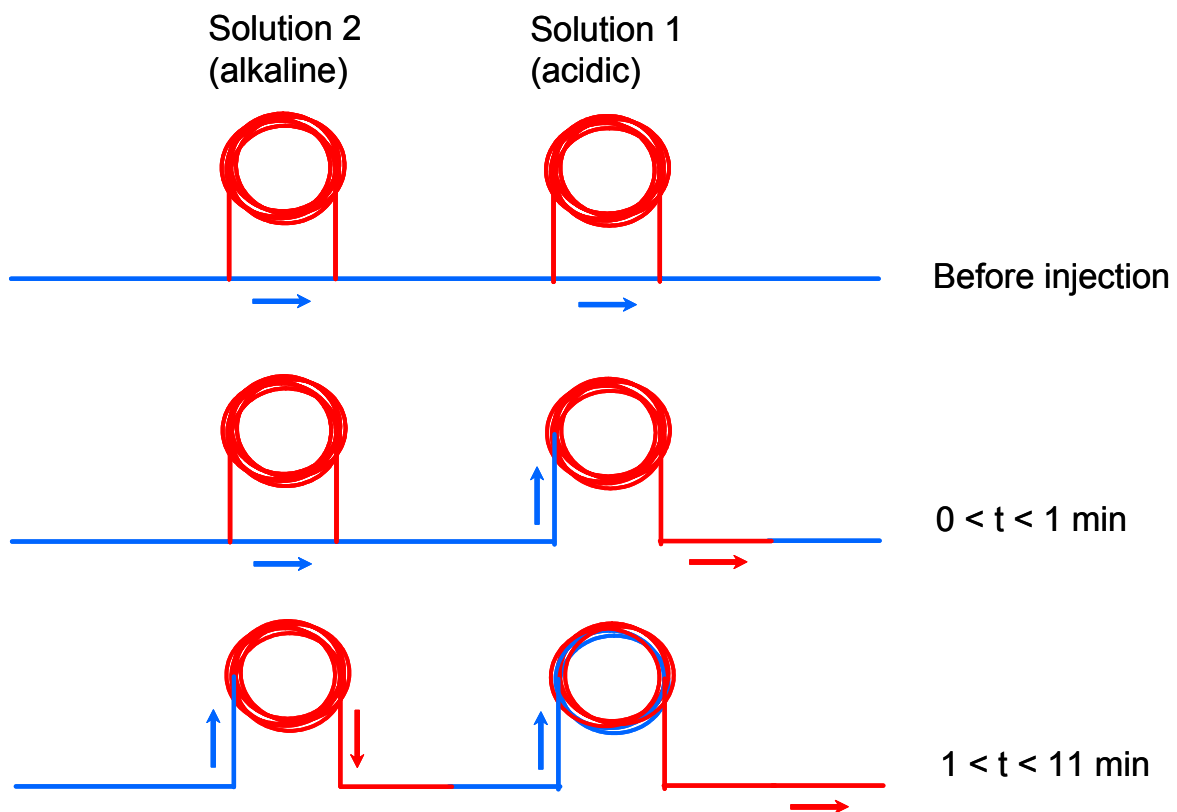


Figure 10. Principle of injection procedure. At time $t = 0$ the tubing loop containing the acidic stock solution 1 is switched into the circulation and at time $t = 1$ min the alkaline solution 2 is switched into the circulation.

The injection valves used were placed as the last equipment at the end of the circulation loop before the exiting outflow to the borehole sections (see Figure 4). This was done in order to minimise the volume and to avoid mixing of the pulses with stagnant water before entering the borehole sections.

Performance of injection

At the LTDE test site the stock solutions were taken through the airlock into the glove box together with the injection loops. The specific tube volumes had been determined in advance at Baslab. The stock solutions were transferred to the injection loops with help of syringes. A procedure was developed whereby the only residual of the stock solutions were left in the vessels, and could easily be returned to Baslab for sampling and determination of the non-injected amount of radioactivity. A detailed description of the transfer and injection procedure is given in Appendix B.

The plan for injections was to first inject solution 1 and after one minute inject solution 2, in order to avoid mixing of the solutions in the tubing. After an additional time of 10 minutes loop 2 was disconnected from the circulation and four minutes later loop 1 was disconnected from the circulation.

2.3.3 Sampling

In addition to the on-line HPGe measurements of the circulation loop, sampling of small volumes of water (~12 ml) was done for subsequent analysis at Baslab. A detailed description of the sampling procedure is given in Appendix B.

2.3.4 Measurements at Baslab

HPGe

The radioactivity concentrations of the γ -emitting radionuclides were measured using an HPGe-detector (ORTEC, relative efficiency 35%). 1 to 10 ml of the samples was transferred to scintillation vials that were filled up with deionised water to obtain a 10 ml geometry.

Liquid scintillation

The procedures used for the measurements of ^{131}Cs are further described in Appendix A.

2.3.5 Calibration of detectors

Prior to the start of the on-line measurements the on-line detector was calibrated with a mixed radionuclide standard solution, Amersham QCY44. The solution was sucked into a loop using a syringe. The calibration measurements on the HPGe detectors were evaluated with the program package Gamma Vision 5.31, (ORTEC), which also was used to determine the efficiency of the detectors and for measurements and evaluation of sample spectra.

The HPGe-detector at Baslab was calibrated with a QCY44 solution. 10 ml scintillation vial geometry was used for calibration and sample measurements.

For the liquid scintillation measurements of ^{131}Cs no standard solution was available. Instead, radioactivity concentration relative to the injected concentration was calculated (C/C_0). The total injected radioactivity of ^{131}Cs was estimated based on an irradiation-decay calculation.

2.3.6 Environmental monitoring

The effective dose rates at the fence and in container 1 were monitored using RNI-instruments according to the description in 2.1.4. The test section (KA3065A03:1) and the first guard section (KA3065A03:2) were monitored as described in 2.1.3 and 2.1.4 in order to detect sudden decreases of radioactivity in the test section or slow increases of radioactivity in the guard section, respectively. Furthermore, the first guard section, which is in primary contact with the test section, was manually sampled to check for leakage from the test section. The pilot bore hole (KA3065A02:3) was also sampled at the end of the experiment.

2.4 Interpretation of tracer test

2.4.1 Simple batch surface sorption model (K_a)

A simple batch sorption model is applied in which sorption is presumed to occur only on the easily available sorption sites on the borehole walls and the stub surface; i.e., no diffusion into the pores of the crystalline rock is considered. Application of the surface sorption concept, the loss of tracer in the water phase can be described as:

$$\frac{C_{\text{aq}}}{C_0} = \frac{1}{1 + K_a A/V} \quad (1)$$

where C_0 is the initial tracer concentration, C_{aq} is the tracer concentration after sorption equilibrium has been obtained, K_a (m) is the surface sorption coefficient, A (m^2) is the geometric surface of the borehole section and the stub surface and V (m^3) is the total volume of water phase (i.e., both the water in borehole section and the water in the circulation loop).

This model approach is experimentally best addressed by determining A/V from the dilution of a non-sorbing tracer injected together with a sorbing tracer.

2.4.2 One-dimensional sorption-diffusion model (K_a and K_d)

For the case of loss of tracer from the aqueous phase caused by diffusion into the pores of the rock matrix surrounding the borehole and the stub surface, a simplified model is used where the diffusion has been approximated to occur in a one-dimensional mode (Byegård et al., 2004). With this model, K_a (m) and K_d (m^3/kg), the matrix sorption coefficient can be evaluated if the diffusion coefficient of the rock is known or estimated from e.g. independent measurements of the porosity. The model is further described in Appendix C.

2.5 Other equipment tests

2.5.1 In touch surveillance functionality tests

The inputs and outputs to the PLC-InTouch system were tested by:

1. Test of reasonableness of input values (note that this is not a calibration).
2. Temporary adjustment of alarm levels in order to trigger alarms.
3. Control of that the desired reaction of an alarm occurs, e.g. stop of circulation pumps in case of a signal from a leak indicator etc.
4. Control of that the alarms are displayed in the alarm list.

2.5.2 Power Supply

The functionality of the battery power supplies (UPS-units) was tested in a separate test. The diesel driven backup generator is tested monthly by Äspö HRL staff.

2.5.3 Alarm system

The coupling of the alarms from the PLC-InTouch system to the Alpha system was tested in combination with the test described in section 2.5.1.

3 Results and interpretation

3.1 Overview of activities

Selection and scoping calculations of possible radionuclides were finalised in early July, 2005. A technical description (Widestrand and Byegård, 2005) of the experiment was accepted by SKB in the beginning of August. Prior to the start of the experiment a number of activities were completed:

- purchase of radionuclides,
- remaining installations at the test site,
- experiment preparations,
- functionality test of equipment,
- development and test of sampling procedures,
- completion of on-call duty lists and alarm instructions
- radiation protection review by the OKG staff including marking of the test site to controlled area.

Radionuclides were delivered to OKG and transported to Baslab by internal transport at OKG. The irradiated ampoules were transported from Kjeller, Norway in a separate road transport conducted by IFE-personnel.

Tracer stock solutions were prepared at Baslab and the injections were done on September 15, 2005. Sampling and analysis was continued to October 12, after which the functionality test was officially terminated in order to let other work in the tunnel proceed (work that potentially could cause pressure disturbances at LTDE were on hold during the functionality test). However, some additional tests and samplings were also done during November. A list of the major events is presented in Table 2.

Table 2. Log of main events during the LTDE pre test.

Date	Time	Event
050905		The power was cut while connecting up the new power supply with diesel aggregate backup. During the power cut the UPS:s were checked. They kept on for 30 minutes. The power system was restarted and some switching was made to supply equipment from the right socket.
050908-09		The electronics of the RNI instruments checked. OK.
050913		Water sample for bacterial analyse from the test section is taken. Calibration of HPGe on-line detector. The part of the test section loop that goes via the on-line HPGe detector is connected to the circulation system on KA3065A03:1.
050915	21.00	Prior to injection of the tracer solutions a water sample is taken from the guard section.
	23.53	Prior to injection of the tracer solutions a water sample is taken from the test section.
	23.55	Injection of the acid tracer solution starts. Valve 15 in injection position.
	23.56	Injection of the basic tracer solution starts. Valve 14 in injection position.
050916	00.06	Injection of basic tracer solution finished. Valve 15 in load position.
	00.10	Injection of acidic tracer solution finished. Valve 14 in load position.
	00.35	The first sample after injection is withdrawn from the test section circulation loop.
	01.15	The second sample after injection is withdrawn.
	06.09	The third sample after injection is withdrawn
	12.00	Water sample no. 1 is withdrawn from the guard section.
	13.40	The fourth sample after injection is withdrawn
050920		Speciation of test section sample by ion exchange resins
050920-051006		Sampling of samples #5 to #10 in the test section
050920-051012		Sampling of samples #2 to #6 in the guard section
050922		Short power cut to LTDE due to diesel generator test. Alarms from RNI and level indicators due to absence of UPS-supply for these channels. Restart of control equipment, RNI instruments, circulation pump and computer LTDE2.
050926		Sampling from the test section through a filter.
051012		Sampling from the test section for analysis of radon and final sample during the undisturbed test period (#11).
051108		Plastic scintillation probe failure (probe gives no pulse output). Probe disconnected for reparation 051124.
051124-25		Additional test section sample #12, guard section sample #7 and sampling of pilot borehole. Additional sample of test section water from pressure cylinder to be compared with sample #12. Calibration performed of pH and redox electrodes in the flow cell done in the glove box. Sampling of tubes for radioactivity measurement and microbe analysis.

Besides the events listed above a continuous logging of the RNI instruments were made as well as logging of data from the flow cell. A daily control of the LTDE test site has also been performed, either on site or reading of files via computer connected to the SKB HRL-net login. In this last case, the video cameras at the test site were used to read, for example, the position of the pressure regulator and the circulation flow in the test section.

3.2 Procedures

3.2.1 Tracer injections

Some of the radionuclides that were planned to be included in the tests according to the technical description (Widestrand and Byegård, 2005) were not actually used in the experiment for different reasons. ^{99m}Tc was said to require a medical permit according to the supplier and could thus not be delivered. ^{64}Cu decayed to a large extent ($t_{1/2} = 12.7$ h) between the time from removal from the reactor to injection, i.e. 4 days. ^{82}Br was not obtained in solution 1 as was planned, the reason for this is not clear. A possible explanation is that due to the nitrate media used the bromide was vaporised and driven off as Br_2 gas in the drying stage of the preparation of the target. ^{135m}Ba was produced in much lower quantities than originally calculated due to delivery from the supplier of the ^{134}Ba isotope in a non-soluble chemical form of, probably, BaSO_4 instead of BaCO_3 . This made the dissolution of the salt difficult already in the first preparation of the ampoule prior to the irradiation. Thus, the ampoule contained very little or no $^{134/135m}\text{Ba}$. A small amount of the fission product ^{140}Ba was produced from fission of U which only to a slight extent compensated the loss of ^{135m}Ba .

The preparations of the stock solutions at Baslab, the transport by car to Äspö HRL and the transport through the airlock into the glove box were done according to the plan. However, the work to transfer the stock solutions from the vessels to the tubing loops was hindered by the central position of the flow cell in the glove box. The flow cell placement made it necessary to work with one hand only which was extremely difficult. Therefore the box door on the right side had to be opened.

The flow cell was placed centrally in order to facilitate calibration; however it needs to be placed in the inner right corner as was originally planned. The recommendation is to rebuild the stand so that the flow cell can be easily disconnected from the stand and moved from the corner placement to the central placement on occasions of calibration.

The injections were done as described in section 2.3.2. The second injection loop contained some nitrogen gas, which caused a pressure dip at the injection. The nitrogen gas was probably sucked in during the transfer of the solutions from the vessels by moving the tube end over the solution surface. With a changed placement of the flow cell as described above, better control of such operations can be achieved by easier handling and better visibility in the glove box.

Mixing in the test section (KA3065A03:1)

The circulation time was approximately 30 to 40 minutes as can be seen in Figure 11 where the injected pulse is shown passing the GM-probe several times after the injection. The monitor showed a peak after less than 1 day elapsed time, see Figure 12, but this was not the true time needed to obtain a good mixing of the section since the GM-monitor measures the actual gamma-emissions without time-corrections for the decay. It can be seen below in the concentration – time curves of the tracers (section 3.4) that approximately 2 weeks circulation time was needed to obtain peak values of all tracers (the strongly sorbing tracers peak earlier than the inert tracers due to the concentration decrease caused by the sorption).

The reason for the slow mixing is likely the existence of poorly mixed zones within the system such as the volume in the pressure regulating cylinder, the slimhole ends and large parts of the stub surface where only diffusion exchange of water and tracers can take part with the flowing water (the water enters the stub section in the middle of the stub and leaves in a tube placed in the periphery).

The slow mixing in the test section is of minor importance for a sorption-diffusion test that will last for several months or more. However, the use of the KA3065A03 borehole for short term tests (hours to days) such as those described in the In situ K_d -report (Byegård et al., 2004) is not recommended since the slow mixing complicates the evaluation in such a case.

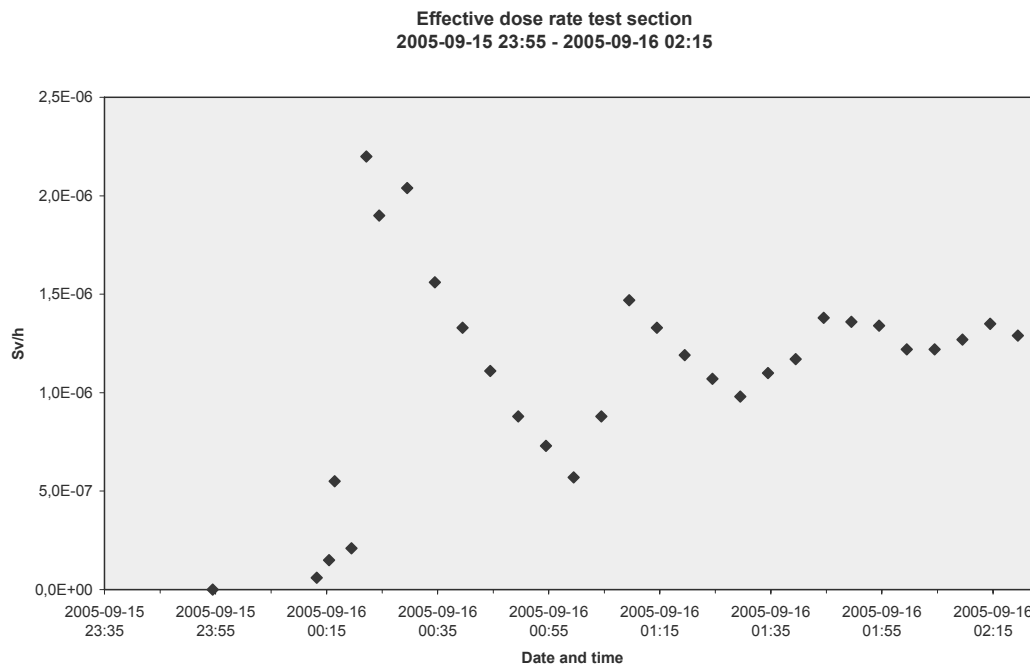


Figure 11. Initial peaks from the circulating pulses in the test section as monitored by the GM-probe.

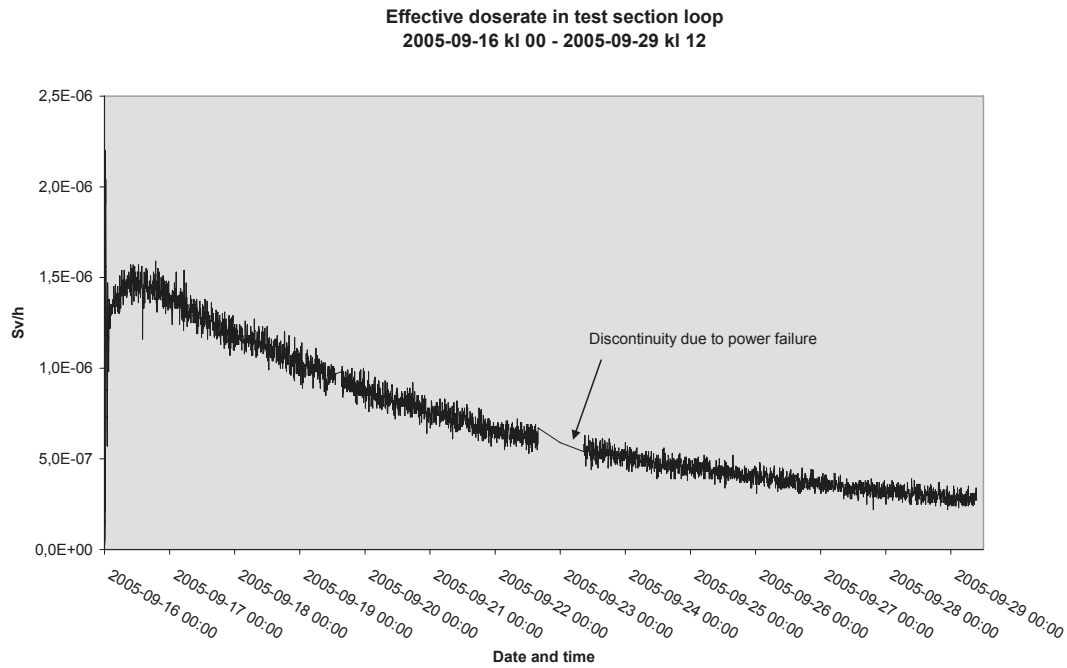


Figure 12. Effective dose rate during the first two weeks after injection.

3.2.2 Samplings

A total of 12 samplings of the test section groundwater were done according to the procedure described in Appendix B. In addition, a sample was taken directly before the injections as a reference groundwater without tracers. A written instruction for sampling has been used and the sampling method worked as planned, however, the operation of the needle valve requires some practical training in order to keep the pressure disturbances low.

Sampling of the first guard section was done 7 times and of the pilot borehole once at the end of the experiment. This sampling was done by opening of a sampling valve for each circulation system in the cabinet outside container 1.

At two sampling occasions the pressure decreased below the set alarm level (28 bars), once in the test section and once in the guard section. The pressure needed to be re-established by the pressure regulator but the power to the pressure regulator was disconnected by an automatic function in the PLC-InTouch system as long as the pressure was below the alarm level. Therefore the power to the pressure regulator could not be turned on again before the pressure was raised above the alarm level (or possible if the alarm level would be adjusted temporarily to a level below the actual pressure). The situation was solved both times by pressurising the system with the shortcut available to the guard section. However, this automatic function should be redesigned so that this situation can be avoided, since the pressure regulator is much faster to increase the pressure than manual valve operations with the shortcut to the guard section.

3.2.3 Valve operations in the circulation systems

The circulation systems consist of a number of valves and attached units, and the space in the glove box is densely packed with equipment. It has been noted during the tests that the use of pre-planned checklists and instructions is beneficial to minimise the risk for practical mistakes in different operations. Check lists should be revised for the start of the long term diffusion experiment.

3.3 Chemical speciation of tracers

3.3.1 Groundwater chemistry measurements

The groundwater samples taken in the test and guard sections directly before the injection 2005-09-15 were analysed by the SKB contracted laboratory. The complete analysis results are presented in Appendix D and E. A sample containing radionuclide tracers (2005-11-24) was analysed at OKG Nuclear Power Plant (Chemistry Laboratory O2). The results are shown in Table 3. The results show an increased salinity in the test section groundwater after injection, which partly can be explained by the Na, Ca, Cl and SO₄ content of the stock solutions. However, the charge balance is about 8% negative for the 2005-11 sample. This sample was measured using ion chromatography and the sample was diluted by a factor of 10⁵, which cause an additional uncertainty in the Cl and SO₄ values. A calculation of the Na, Ca, Cl and SO₄ concentration increase in the test section after injection was done based on the contents in the stock solutions. The calculated concentration increases in the test section groundwater from the stock solution injections are 1200 ppm for Cl, 800 ppm for Na, 90 ppm for Ca and 90 ppm for SO₄. Thus, the concentration increase caused by the injection can only partly explain the high concentrations of the 2005-11-24 sample.

Table 3. Major components analysis of test section sample after injection sampled 2005-11-24 (OKG laboratory), test and guard section samples before injection 2005-09-15 and comparison with sampling January 2004 (SKB contracted laboratories).

	2005-11 (OKG)	2005-09 (SKB)	2005-09 (SKB)	2004-01 (SKB)	
	Test section after injection	Test section before injection	Guard section	Test section	
Cl	8 700	5920	6150	7 020	ppm
SO ₄	900	409	940	417	ppm
Mg	50	46	45	42	ppm
K	10	11	11	12	ppm
Ca	2 170	1870	1880	2 030	ppm
Na	2 660	1900	1900	2 070	ppm
pH	7,5	-	-	7,3	

3.3.2 Speciation of tracers by ion exchange resins

As a part of the effort obtaining speciation information concerning the tracers in the groundwater, ion exchange studies were performed. Two ion exchangers were prepared, one containing 1 ml strongly basic anion exchanger, Amberlite (16-50 mesh) and the other containing 1 ml strongly acidic cation exchanger Dowex 50W x4 (sodium form). During the sampling, first ~5ml was slowly (1 droplet per 5 seconds) passed through the anion exchanger, i.e., taking the groundwater directly from the sampling valve to the ion exchanger. The eluted water was collected in a scintillation vial and was later measured for its tracer content (γ -spectrometry and ^{131}Cs analysis according to the procedures described in section 2.3.4). After that, the mentioned procedure was repeated for sampling through the cation exchanger. Directly before the sampling through the ion exchangers, a regular sampling had been performed.

The results of the ion exchange speciation is presented in Table 4 and are given as concentration decrease of the tracers in the eluates from the anion and cation exchangers, given in relation to the concentration in the non-processed sample..

Regarding the results for the presumed cations, the Cs(I), Ca(II) and Lu(III) interact as would be expected from a cationic form; more or less completely sorbed in the cation exchanger and passing through the anion exchanger. There are, however, some indications of losses of especially Lu(III) in the anionic exchanger which possibly could be caused by the existence of e.g., a negatively charged carbonate complex species, cf. section 3.3.3. Nevertheless, the very different behaviour and also expected behaviour of the presumed cations in the cation exchanger and anion exchanger, respectively, should be regarded as a proof of none or very little existence of colloidal forms for these tracers.

The obtained result for the speciation of iodine is difficult to explain. Not more than 56% of the I(-I) is found to sorb on the anion exchanger. However, one should be aware of that the high concentrations of Cl^- (together with the pre-saturation of the anion exchanger with Cl^-) might act as an effective competitor for the sorption of I^- on the anion exchanger. If there is not very much higher selectivity for I^- versus Cl^- this could be a possible explanation for that the I(-I) is not completely adsorbed by the anion exchanger.

What is even more difficult to explain is the indication of adsorptive loss of I(-I) in the cation exchanger (29%). This observation together with the unexpected indications of sorption of I(-I) in the total experiment, illustrates the difficulties of using I(-I) as a non-sorptive tracer, a problem reviewed by e.g., Behrens 1982.

The Cd(II) tracer is almost completely adsorbed in the cation exchanger. Although the chemical speciation calculation below indicates an existence of chloride complexes, it is obvious that the binding to the cation exchanger is strong enough to compete out the complexation or that the chloride complexes are adsorbed in the cation exchanger. The large amount of adsorption of Cd in the anion exchanger is more difficult to explain. One could speculate of the possibility of Cd forming surface complexes in the anion exchanger with the chloride loaded on the anion exchanger. No solid proof for this theory can, however, be delivered.

Np(V) is not to any significant amount adsorbed in the anion exchanger, which is in line with the expected species (NpO_2^+) of that compound. However, it is somewhat unexpected that not more than 55% of the Np(V) is adsorbed in the cation exchanger. A possible explanation to this is that the competition from naturally present high concentrations of cations in the groundwater (e.g., Na^+ and Ca^{2+}) and that the selectivity for monovalent NpO_2^+ binding to the cation exchanger is not high enough to allow a full adsorption.

No result was obtained for Hf(IV). This was because the concentration had already decreased to very low amount and that not sufficient measuring time was available for the γ -spectrometry measurement of the ion exchange processed samples to obtain enough counting statistics for ^{181}Hf .

Table 4. Speciation of tracers using ion exchange resins.

Tracer	Concentration (M)	Sorbed in cation exchanger	Sorbed in anion exchanger
I(-I)	Carrier free	29 %	56 %
Cs(I)	1E-8 (nat.)	99 %	13 %
Ca(II)	0.05	>98 %	<1 %
Cd(II)	1E-7	94 %	71 %
Lu(III)	2E-10	>91 %	25 %
Hf(IV)	2E-7	Not speciated	
Np(V)	Carrier free (U – 2E-7)	55 %	2 %

3.3.3 Geochemical speciation calculations

Cd and Np

Preliminary geochemical speciation calculations regarding Np and Cd have been performed. The program PHREEQC (Parkhurst and Appelo, 1999) was used in the calculations together with the database files from Yoshida and Shibata, (1999) and Allison et al., (1990), used for Np and Cd, respectively. In the calculations the groundwater composition from KA3065A03, dated 2004-01-21 was used.

The speciation calculations for Np aimed to see the distribution of the species as a function of the redox potential, Eh. The preliminary results can be seen in Fig. 13, which indicate that Np(V) is the dominant oxidation state above ~100 mV. The Np(V) species are known to sorb very weakly (Carbol and Engqvist, 1997) and this may explain the high ^{239}Np concentration observed in the present LTDE functionality test. The concentration of Np in the calculations was 1 μM . This is a quite high figure, a more realistic one should probably have been 2-3 orders of magnitude lower. In the calculations $\text{NpO}_2(\text{am})$ was found to be oversaturated, which could be explained by the high concentration of Np. One calculation at +100 mV and with an Np concentration of $1 \cdot 10^{-8}$ M, $\text{NpO}_2(\text{am})$ was found to be undersaturated.

Distribution of Np species as a function of Eh.
GW from KA3065A03, 040121

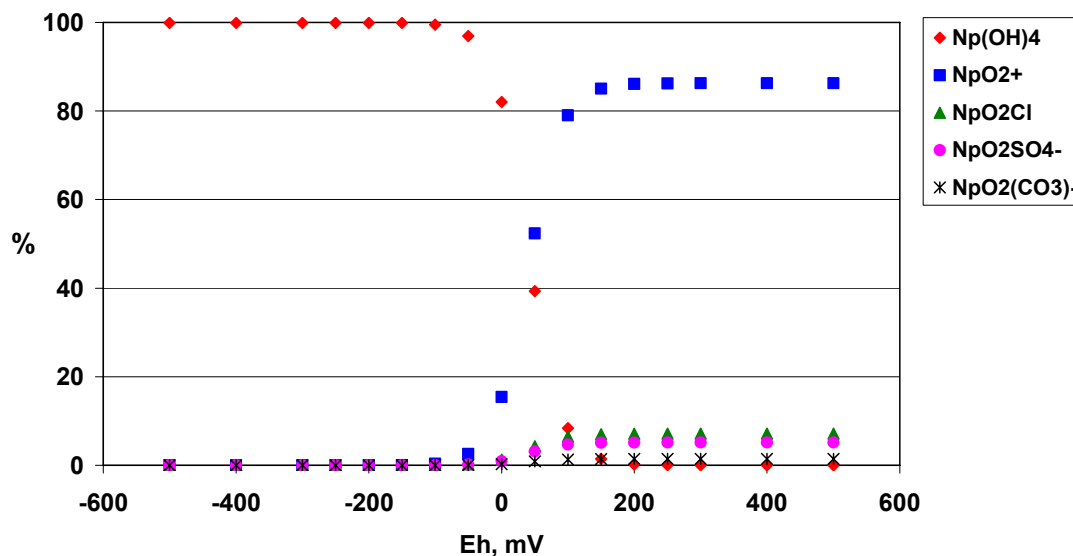


Figure 13. Geochemical speciation calculations for Np with the use of PHREEQC (Parkhurst and Appelo, 1999).

The purpose of the speciation calculations for Cd was to investigate to what extent this tracer formed complexes with chlorine. The Cd concentration in the calculations was set to the same as the experimental concentration, i.e. 4×10^{-7} M.

The preliminary results indicate that CdCl^+ (60%) is the dominating species followed by CdCl_2 (24%) and Cd^{2+} (12%). See also Fig. 14. According to the calculations, the high chloride concentration make chloride complexes to effectively dominate over other complexes.

Distribution of Cd in GW from KA3065A03, 040121

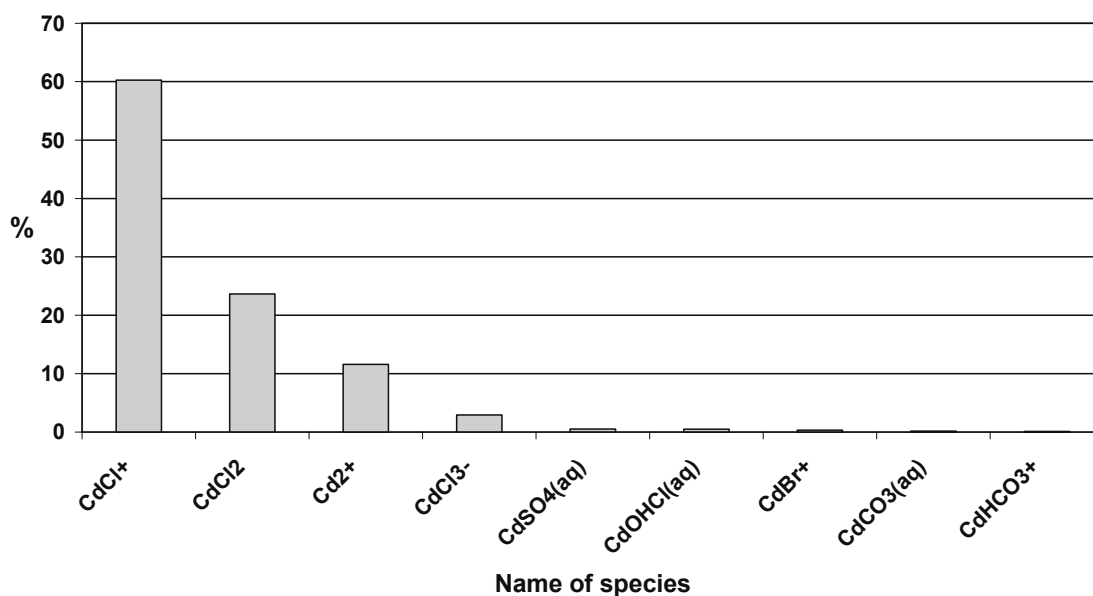


Figure 14. Geochemical speciation calculations for Cd with the use of PHREEQC (Parkhurst and Appelo, 1999).

Lu and Hf

In addition to the above mentioned speciation calculations, preliminary speciation calculations for Lu and Hf were performed. In these calculations the LLNL database (LLNL, 2005) was used together with PHREEQC (Parkhurst and Appelo, 1999). The LLNL database is accompanying the PHREEQC - Version 2.12.1 November 16, 2005 (Charlton and Parkhurst, 2002) package, available from USGS. The tracer concentrations used in the calculations for Hf and Lu was taken from Table 4.

The results for Lu indicate the following dominating species: LuCO₃⁺ (68 %) and Lu³⁺ (20 %). Further, the result indicates presence of the species Lu(CO₃)₂⁻ (5 %) that, to some extent, might explain the loss of Lu in the anion exchanger, cf. Table 4.

According to the preliminary results obtained for Hf the dominating species was Hf(OH)₅⁻ (100 %), which might be doubtful since only three species were listed in the database: Hf(OH)₅⁻, Hf⁴⁺ and Hf(OH)₃⁺. The Hf(OH)₅⁻ complex would also be expected to be non-sorbing. However, if the sorption or surface complexation of Hf(IV) is stronger than the formation of the aqueous Hf(OH)₅⁻ complex, sorption can still occur since the equilibria then would be shifted towards the surface reactions.

3.3.4 Radon sampling and analysis

In order to estimate the radon concentration in the groundwater a 5 ml water sample was taken. The sample was directly transferred from the sampling valve to a vial with 15 ml Ultima Gold AB liquid scintillation cocktail of special purpose for alpha/beta discrimination counting. The sample was measured at Baslab using the Wallac instrument. The sample radon concentration at the time of sampling was 35 Bq/L, which

is low compared to typical values of fracture samples at Äspö (typically 200 to 1000 Bq/L, see e.g. Byegård et al., 2002). However, the surface to volume ratio in KA3065A03:1 is much lower than in fractures, i.e. that the radon is diluted more in the test section than in other boreholes.

The radon emanation (outflow) from the surfaces in the test section have been calculated based on the known surface areas, volume and radon concentration. It should be noted that this is a simplified approach; a more correct approach should probably include matrix diffusion estimations for the migration of the produced radon. The radon emanation is presented in Table 5 together with a comparison of other materials.

The result in the test section is relatively high compared to the other materials that were measured in the laboratory. Compared to the laboratory measurement of fracture specific material, the production rate in the in situ experiment is >60 times higher. The large discrepancies can be seen as an indication that laboratory experiments for estimating radon emanation not fully mimic realistic conditions. Since radon emanation is a process analogous to matrix diffusion, the results of radon emanation can be useful when evaluating the final diffusion experiment.

Table 5. Radon emanation from different materials at Äspö HRL.

Sample	Radon emanation (Atoms $^{222}\text{Rn} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$)
<i>LTDE stub and slimhole surfaces:</i> KA3065A03:1 2005-10-12	600
<i>Laboratory experiments with crushed materials</i> (SKB IPR-02-68):	
Fine-grained granite (Äspö HRL)	160
Äspö diorite (Äspö HRL)	10
Mylonite Feature A TRUE-1	<11

3.3.5 20 nm filtered sampling

The 20 nm filtered sample (Whatman Anotop 20 nm) showed no clear differences in concentrations neither relative the previous and following samples nor to the on-line measurements (see Figure 16). Consequently, sorption to colloidal particles or microbes in the groundwater larger than 20 nm is not indicated to occur to any major extent.

3.3.6 Microbe analysis

The water sample analysed for microbes shows an average value of 3.3×10^5 cells per ml. This is 6 times lower than was measured at LTDE in 2002, but much higher than the value obtained after equipment cleaning and flushing of the borehole in 2003 (about 1×10^3 cells per ml). The value is relatively high for deep groundwaters, but not unusual, for this depth (see Figure 15 for a comparison of measurements). One of the microbe types was large, which indicates that it was growing and lived under “good conditions” (Pedersen, 2005)

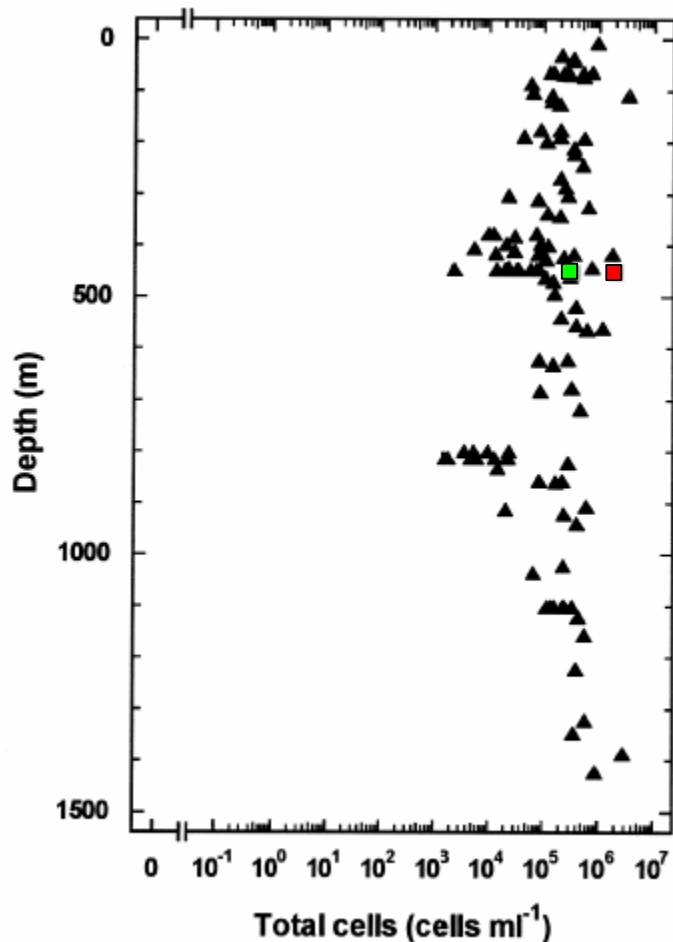


Figure 15. Placement of the bacteria measurement at LTDE in September 2005 (green square) and December 2002 (red square) in a matrix from other deep groundwaters.

3.4 Tracer concentration measurements

3.4.1 Injected radioactivity

The total amounts of injected radioactivity are presented in Table 1. The injected radioactivity is calculated based on the difference measurements of the amount of radioactivity that was transferred from the stock vessels to the injection loops. 95% of solution 1 and 99% of solution 2 were transferred and injected, the remainders were returned to Baslab in the original stock solution vessels.

3.4.2 Tracer concentration-time curves

Relative concentration versus time curves for on-line and laboratory measurements of radioactivity concentrations are shown in Figures 16 and 17. Maximum concentrations of the inert or weakly sorbing tracers are reached after about 2 weeks elapsed time. Poor mixing in parts of the equipment such as in front of the stub surface and the pressure regulator cylinder is a likely cause for the late peaks.

Observation of the relative concentrations at 13 days show an increase in sorption strength in the order $\text{Ca(II)} \leq \text{I(-)} < \text{Np(V)} < \text{Cd(II)} < \text{Cs(I)} < \text{Lu(III)} < \text{Hf(IV)}$. The trend generally follows the charge of the major species of the sorbing complexes. Ca is non-sorbing in the relatively saline water and weak sorption of iodine is observed. Week sorption of iodine has been observed earlier at Äspö in e.g. the STT1-b test within the TRUE-1 experiments (Widestrand et al., 2001). On the other hand, inert behaviour of iodine was observed in the TRUE BS continuation project (Andersson et al., 2005). It was suspected that the different behaviour of iodine was caused by sorption on equipment materials in the TRUE-1 experiment. The high redox potential gives Np(V)O_2^+ as major Np-species which is known to sorb weakly compared to the Np(IV) which undergoes hydrolysis and sorbs strongly. Cadmium chloride species dominate the Cd speciation which corresponds well to the intermediate sorption of Cd. Lu and Hf are expected to be strongly hydrolysed and also show a relatively strong sorption. Cs sorption is relatively strong which is in accordance with earlier field test observations. $^{140}\text{Ba(II)}$ data was relatively uncertain due to the low activity amount of the tracer. An uncertainty analysis indicated that Ba(II) was non- or weakly sorbing (less sorbing than iodine).

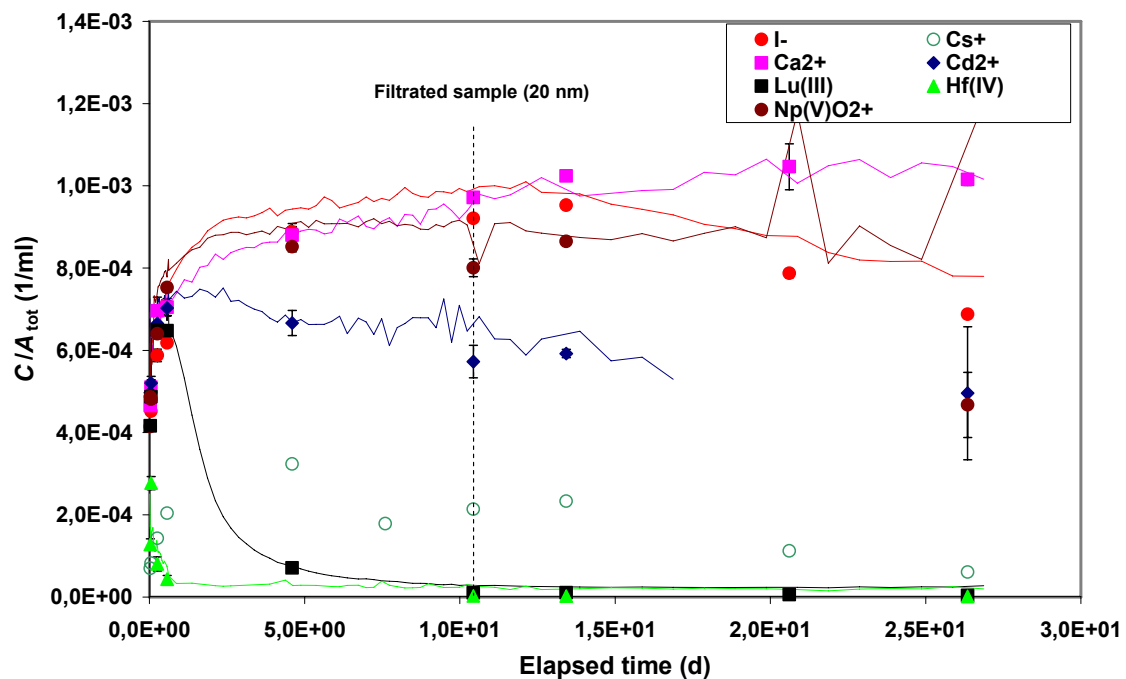


Figure 16. Relative concentration versus elapsed time curves for samples (dots) and on-line measurements (lines) in linear scale. The radioactivity concentration is divided by the total activity injected.

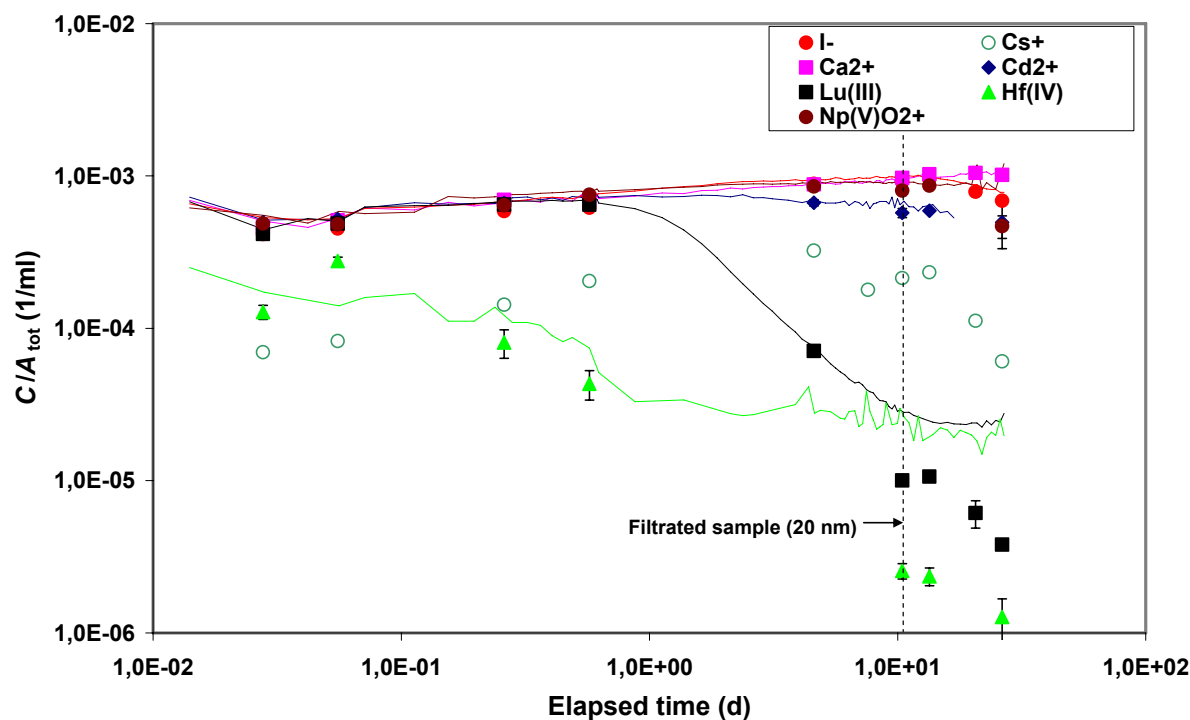


Figure 17. Relative concentration versus elapsed time curves for samples (dots) and on-line measurements (lines) in logarithmic scale. The radioactivity concentration is divided by the total activity injected.

3.4.3 Sorption on tubing

Sorption of the only remaining (non-decayed) tracer Hf on tubing was measured on a ~20 cm tubing sample. A slight sorption of about 5 to 10 Bq/m was observed after 2 months, which corresponds to about 0.5 to 1 kBq for an estimated total tubing length of 100 m. The total injected amount of Hf was 14 kBq and after 2 months >99% of Hf was sorbed. Consequently, only a minor part of the Hf, which was the most strongly sorbing tracer used, is estimated to be sorbed on the tubing (<7% of the sorbed amount). An indication of the sorption on the tubing can also be seen in Figure 17 where the concentration determined in samples and on-line differs for Hf and Lu at the end of the experiment.

3.4.4 Evaluation of surface sorption (K_a) with simple batch sorption model

Surface sorption coefficients were evaluated as described in section 2.4.1 assuming that all sorption occurred on the geometrical surfaces of the stub surface and the borehole wall in the slimhole. The data are presented in Table 6 below.

3.4.5 Evaluation of surface sorption (K_a) and matrix sorption (K_d) with one-dimensional diffusion model

Surface sorption coefficients and matrix sorption coefficients were evaluated as described in section 2.4.2 and Appendix C. The pore diffusivity was calculated using Archie's law based on an assumption of 0.5% rock matrix porosity and using water diffusivities for the different species. K_d was the only fitting parameter and K_a was calculated based on K_d/K_a ratios obtained from the TRUE BS-project. The fitting of the model was done to the concentration decrease at 28 days, i.e. only one data point was modelled. The results are therefore only indicative and should not be regarded as absolute values. The data are presented in Table 6.

Table 6. Preliminary sorption data from very basic evaluations of the functionality tests. These data should be regarded as indicative and should be used with precaution before a deeper evaluation including modelling of the whole data sets is done. Evaluation was done after 28 days. Note that the diffusion model was fitted to the 28 day data point only, i.e. that the whole data set was not modelled.

Tracer	Batch model	Surface sorption / Matrix diffusion model		TRUE BS Continuation (batch sorption experiments on rim zone material, Byegård and Tullborg 2006)
	K_a (m)	K_a (m)	K_d (m ³ /kg)	
I(-I)	8E-3	Not modelled		-
Cs(I)	3E-1	0.2	0,27	$K_a=(1-10)E-3$ m $K_d=(1-10)E-3$ m ³ /kg
Ca(II)	(<3E-4) ^{B)}	Not modelled		$K_a=(2-3)E-5$ m ^{A)} $K_d=(2-100)E-6$ m ³ /kg ^{A)}
Ba(II)	(<6E-3) ^{B)}	Not modelled		$K_a=(6-8)E-4$ m $K_d=(2-50)E-4$ m ³ /kg
Cd(II)	2E-2	1.3E-2	1,6E-2	-
Lu(III)	4	4.3	5	-
Hf(IV)	13	13	15	-
Np(V)O ₂ ⁺	2E-2	1.6E-2	2E-2	-

A Value is obtained from sorption experiments using the analogous tracer Sr²⁺

B Estimated maximum value based on measurement uncertainty. Note that sorption was too weak to be statistically verified for Ca and Ba.

3.5 Test section volume estimations

Calculation of the test section volume based on the measured dilution of the tracers gives a volume of 930 to 970 ml at 80% filled pressure regulating cylinder which corresponds to a maximum volume of 1030 ml. The geometrical calculations performed estimates the volume to 880 to 950 ml at 80% filled cylinder and 960 to 1030 at 100% which agrees well with the dilution measurement.

A rough calculation of the circulated volume based on the circulation time of the injected pulses (35 to 40 minutes) and the flow rate (16 ml/min) gives a circulated volume of 600 ml. This indicates that stagnant volumes are existing which is also indicated by the relatively long time needed to obtain a good mixing in the system.

3.6 On-line measurements of E_h and pH

Measurements of pH and E_h were performed during a two months period (Figures 18 and 19). The electrodes were calibrated before and after the measurement and the difference for the reference electrode was found to be less than 10 mV, which is an acceptable normal drift considering the time span. At the time of the final calibration the redox potential had decreased from the initial 500 mV to 200 mV (gold) and 100 mV (platinum) and continued decreasing slowly. However, the first measurements after an exchange of test section groundwater and a final calibration indicates an increasing redox potential (not shown in figure). The relatively high redox potential at the termination of the measurement and the indication of increasing redox potential after the final calibration causes doubts regarding the possibility to reach low enough redox potentials for reduction of redox sensitive tracers in the test section.

Oxidation of minerals in the test section during previous exposure to oxygen could be one reason for the slow decrease of the redox potential. The borehole was open and exposed to water in contact with air for a relatively long time (months to a year) between the drilling and the borehole installations. The expected potential would be about -150 mV or lower based on previous measurements in deep boreholes (Wacker et al., 2004), which is far from the lowest observed potentials at 100 mV.

The pH was stabilising at 6.5 during the last weeks of the measurement. One of the glass electrodes was found to be defect and it was excluded from the analysis. It can be noted that the pH measurements on samples presented in Table 3 are typical for Äspö groundwaters (7.3 and 7.5), but the flow cell measurements indicate stable pH at 6.5. It can be questioned which is the correct measurement, or if both methods are correct? Possibly, sampling may cause changes in the sample due to contact with air and degassing which could affect the pH values of the samples. However, the effects are usually not in this magnitude. Measurements in deep boreholes (down to 900 m in depth) have shown that the difference between pH measured on-line in the borehole and pH measured on surface is less than 0.5 units (Wacker et al., 2004). Typical pH values obtained from measurements in deep boreholes range between 7 and 8.5.

The entire system seems to be sensitive to other activities in the glove box, which can be observed as correlated peaks in the plots. The discontinuities in the plots are due to calibration of the electrodes (August 25th), installation works at the test site and flushing of the section with water from the guard section (September 6th and 7th). A possible disturbance is static electrical fields which is often observed by adhesion of plastic bags, papers etc onto the gloves in the box. There is a possibility that the measurement system is affected by other power sources, for example the circulation pump. However, no electrical disturbances from the pump motor or electrical cables were observed in a previous workbench test.

A new position of the flow cell at the back of the box may reduce such disturbances. If that does not help, the flow cell may need a metal shielding.

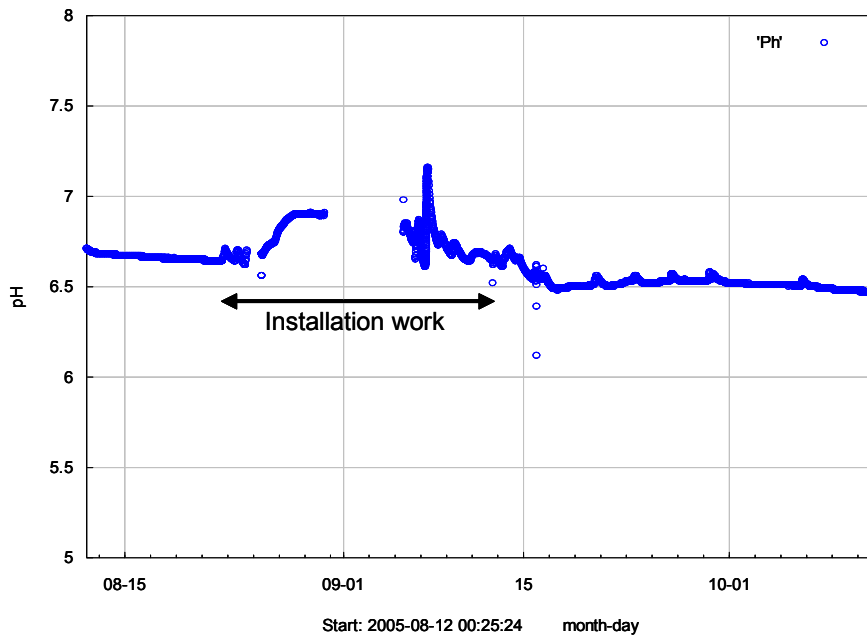


Figure 18. pH measurement in section KA3065A03:1 2005-08-12 – 2005-10-12. The period marked by the arrow was affected by installation works. The small peaks in the period after 2005-09-15 are correlated to activities in the glove box.

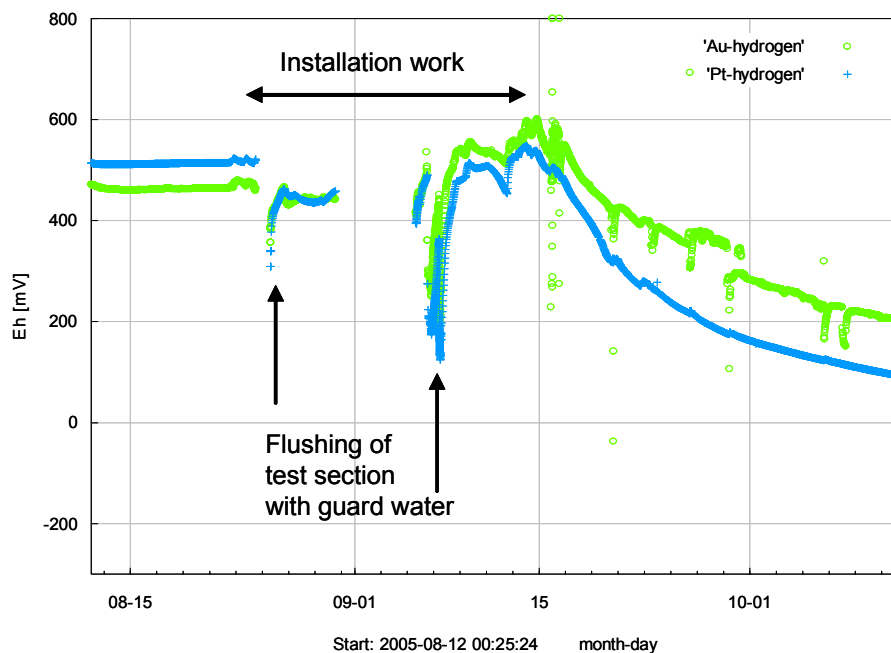


Figure 19. Redox measurement in section KA3065A03:1 2005-08-12 – 2005-10-12. The dips indicated by the vertical arrows were obtained after flushing of the test section with groundwater from the first guard section. When flushing was discontinued and the test section groundwater was circulated only, the redox potential increased again. The Au-electrode was very sensitive to activities in the glove box as can be seen by the many dips in the time period after injection 2005-09-15. The period marked by the horizontal arrow was affected by installation works

The radionuclide solution was injected September 15th. A small decrease in pH was observed shortly after the injection, which could be an effect of not obtaining a complete neutralisation of the firstly injected acidic stock solution (Fig 20).

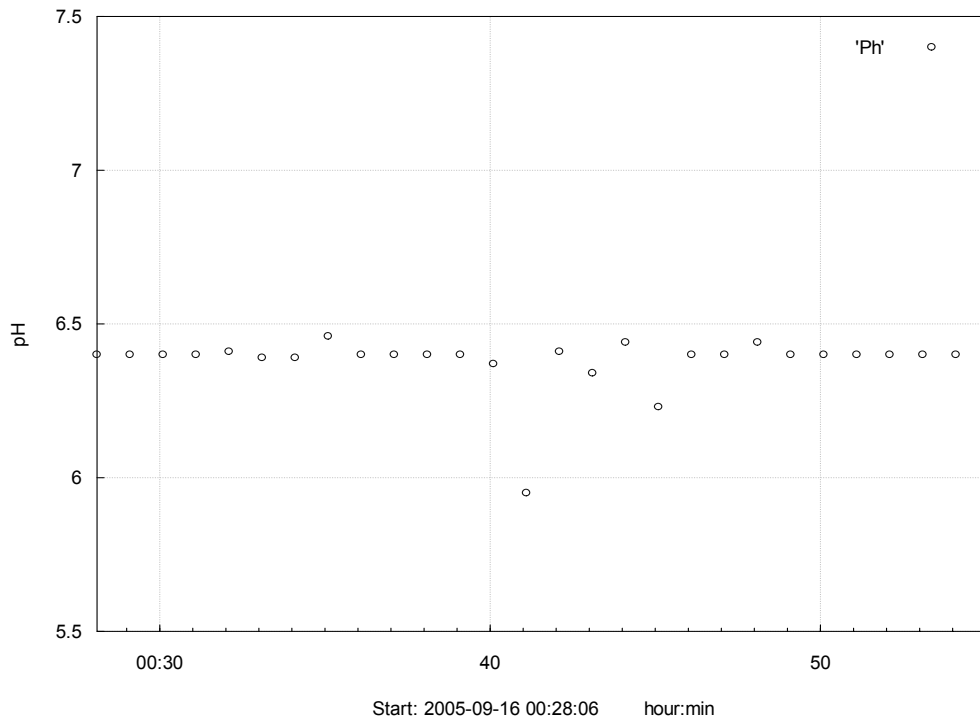


Figure 20. pH measurement during the time of injection.

3.7 Pressure monitoring and control

All isolated borehole sections involved in the LTDE project are connected to the Hydro Monitoring System (HMS) for pressure monitoring through the PLC.

In Figure 21a and 21b an overview of the pressure in some of the LTDE borehole sections is presented. The experimental hydraulic conditions were stable according to monitoring of pressure, apart from short pressure disturbances. Most of the disturbances, seen particularly in the test and guard sections in KA3065A03, are due to injection and sampling occasions in the borehole. One exception is the drawdown in the end of October, i.e. after the official termination of the functionality test, and is seen in all sections. This is caused by the re-instrumentation in the TRUE-1 boreholes KXTT3 and KXTT4, with the largest response (about 200 kPa) from KXTT4.

The LTDE area is surrounded by two dominating structures, NW-2 and NW-3. The TRUE-1 borehole sections are within structure NW-2', interpreted to intersect with structure NW-2 at the TRUE-1 site. The test confirms the conclusion from the hydraulic pre-tests (Wass, 2005), i.e. the NW-2, NW-3 and related structures are of vital importance for the hydraulic pressure responses in the LTDE boreholes and pumping, drilling etc should not be performed in these structures during the forthcoming long term experiment.

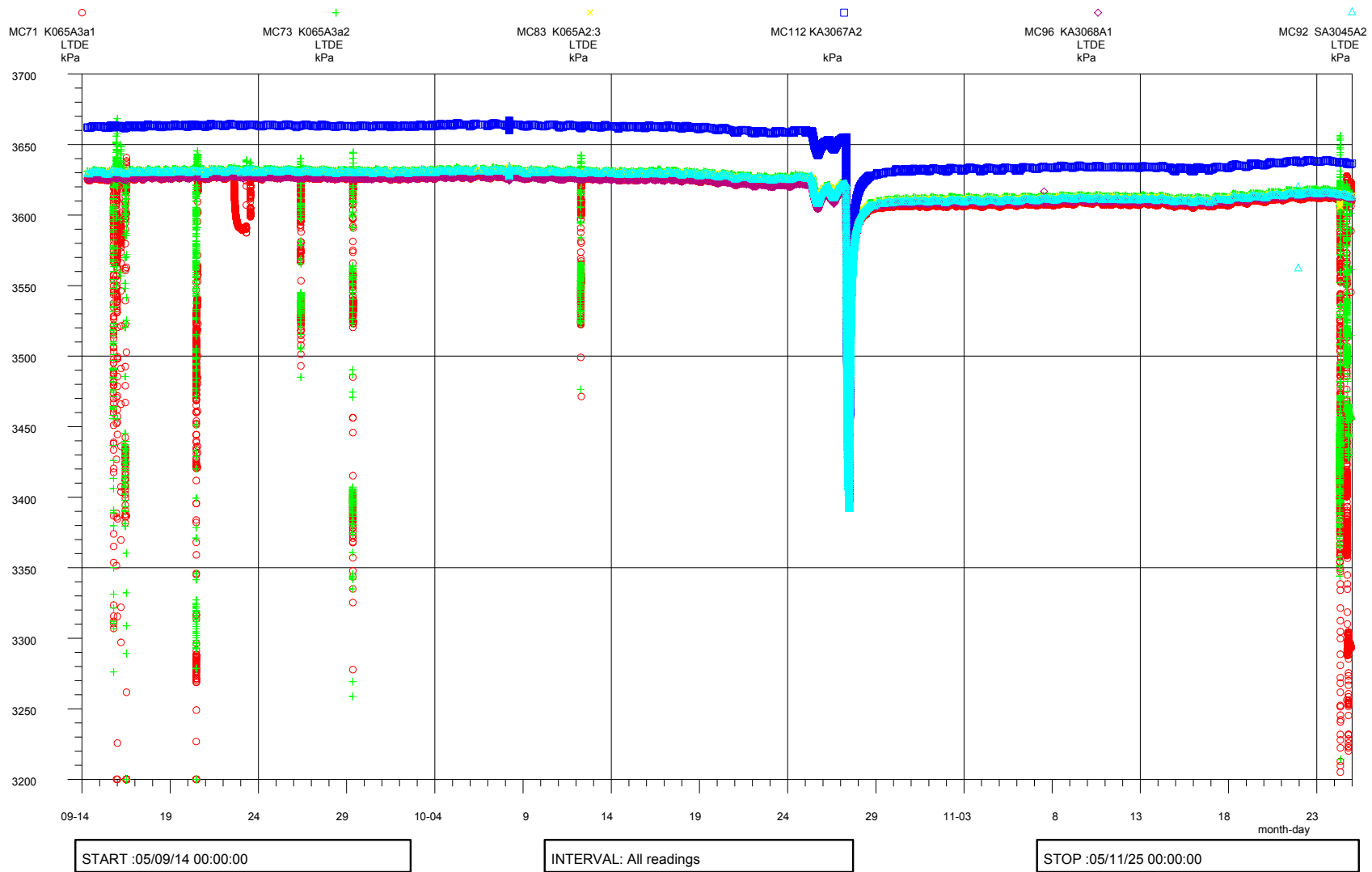


Figure 21a. Pressure in some selected LTDE borehole sections during the period 2005-09-14–2005-11-25. See Figure 1 for borehole locations.

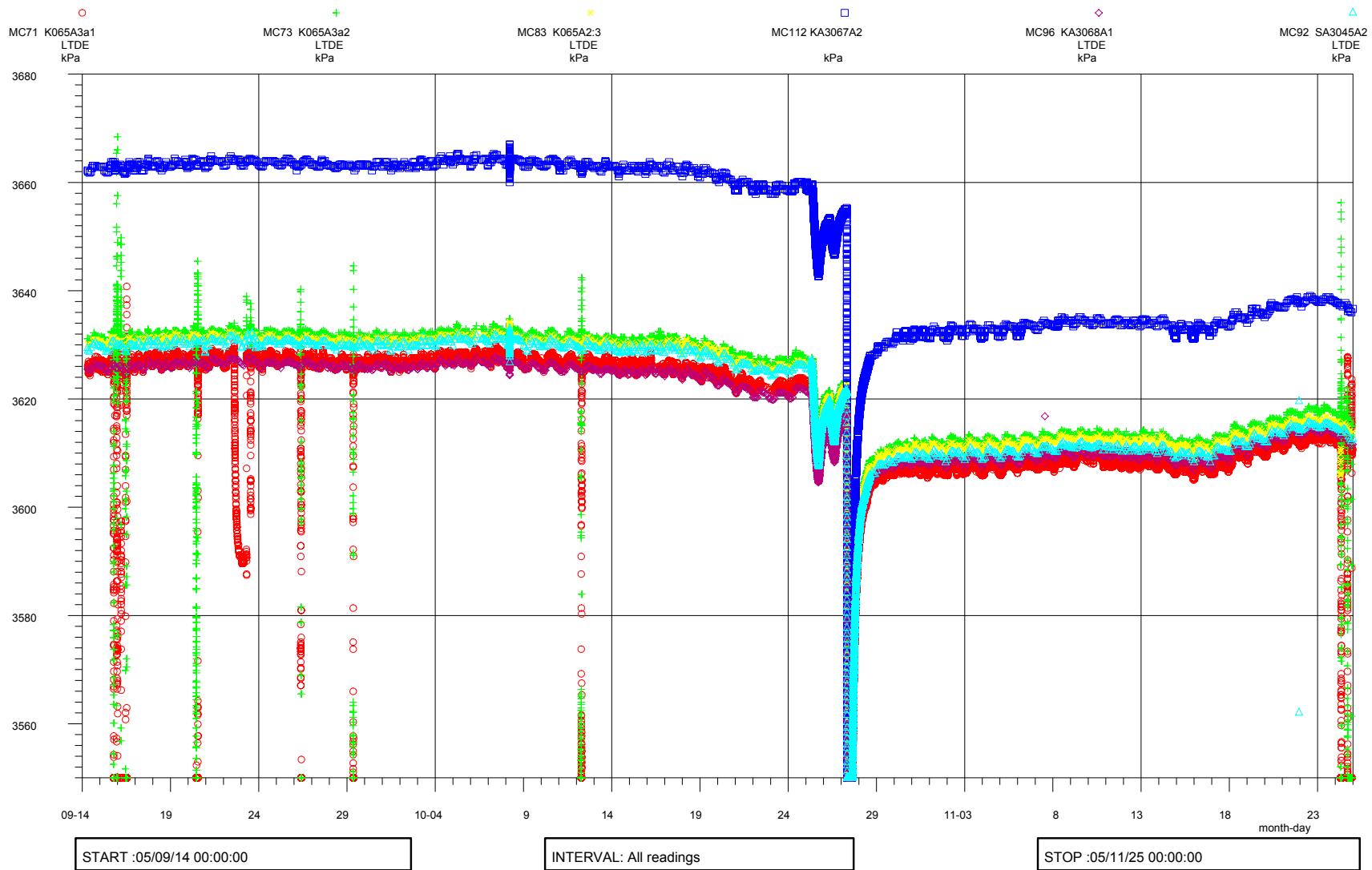


Figure 21b. Pressure in some selected LTDE borehole sections during the period 2005-09-14 – 2005-11-25. Note that the y-axis scale is magnified compared to Figure 21a. See Figure 1 for borehole locations.

The pressure regulator has been in stable operation without failures during the period April to November. Prior to the start of the experiment the cylinder was filled up with groundwater by running the piston backwards to a position of about 100 mm (maximum 500 mm) in order to allow for outtake of sampling volumes during the tests and still to enable pressure regulation to lower pressures if needed.

More detailed plots over the pressure in the test and guard sections in borehole KA3065A03 during injection and sampling procedures are shown in Figure 22. The first injection (acidic injection, valve 15) was made at 23:55 and is not visible in the pressure plot. The second injection (basic injection, valve 14) was made at 23:56 and the following drawdowns around 00:35 and 01:15 are sampling occasions. The pressure dip at the second injection 23:56 was caused by compression of nitrogen gas trapped in the injection loop. Prior to the injection a groundwater sample was taken (approximately between 23:52 to 23:55).

Short pressure responses in the first guard section (KA3065A03:2) is recorded at several times in connection to pressure changes due to sampling- or injections in the test section. It can be seen in Figure 22 (bottom) that the response in the guard section appears both in the beginning and at the end of a drawdown in the test section. It is observed as a pressure decrease following the opening of the test section and as a pressure build-up when the pressure is restored by the piston movement. The reason for this behaviour is likely due to responses through the rubber-cylinder sealing at the stub or from penetrating tubing, i.e. a mechanical disturbance rather than a hydraulic. The pressure in the test section was restored quickly by the pressure regulator after sampling and injections as can be seen in Figure 22.

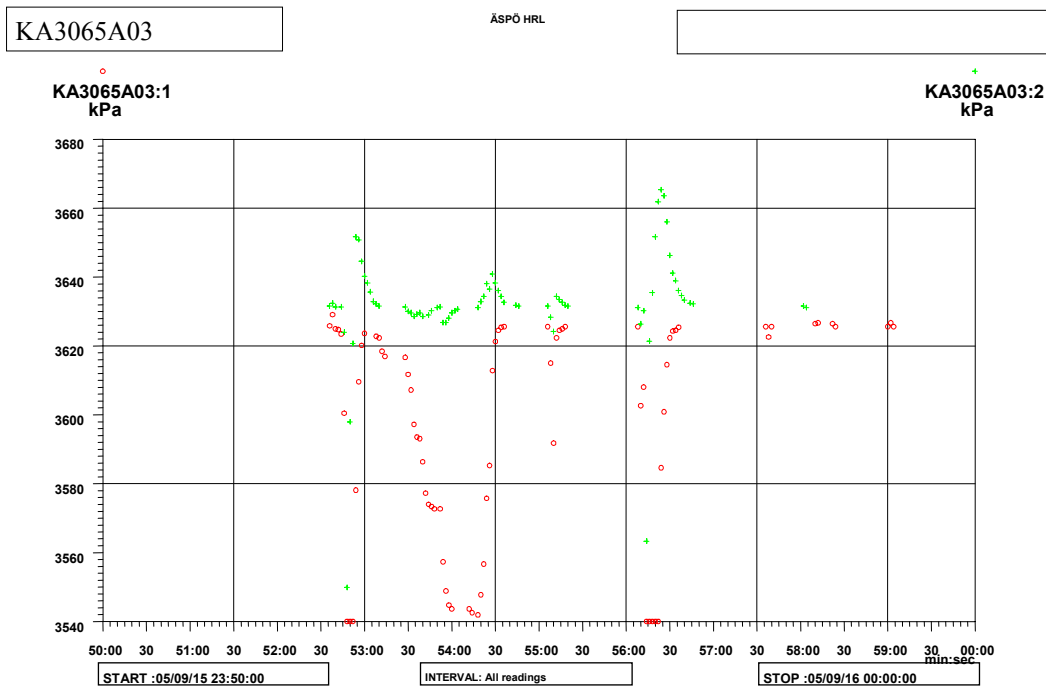
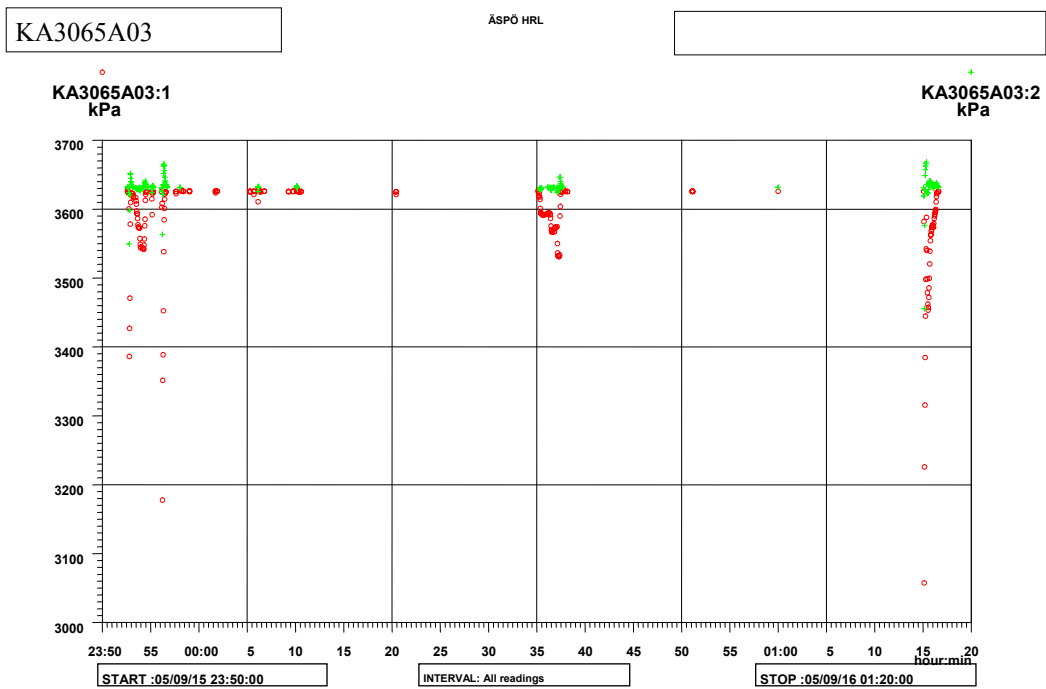


Figure 22. Pressure in test (red circles) and guard (green plus) sections in borehole KA3065A03 during injection and sampling. The top figure shows injections and two samplings in the interval 2005-09-15 23:50 to 2005-09-16 01:20. The bottom figure shows the injection period 2005-09-15 23:50 to 00:00 in detail. Note that the y-scale is from 3540 to 3680 kPa. A water sample is taken from 52:30 to 54:40, the first injection is done at ~55:10 and the second injection at 56:10.

3.8 Environmental monitoring

Guard section

Samples were withdrawn from the guard section in order to detect any potential leakage from the test section into the guard section. The samples were measured at Baslab on the HPGe detector. From the obtained γ -spectra no evidence for leakage could be observed for any of the tracers used. The spectra were also analyzed for MDA-values (Minimum Detectable Activity). The MDA values divided by the total amount of activity injected for ^{131}I are presented in Table 7. ^{131}I is the radionuclide that had the lowest detection limit. The MDA values are time corrected. The volume of the guard section is $10 \text{ L} \pm 1 \text{ L}$ and the sample volumes measured with the HPGe detector was 10 ml.

Table 7. Detection limits for ^{131}I that could be detected by sampling in the guard section in the event of leakage from the test section into the guard section. The values are given as the minimum fraction of leaked radioactivity in the test section that could be detected in the guard section. This can be regarded as a maximum leakage fraction based on the actual detection limits of the different samples.

Date of sample	Nuclide	Time corrected activity/Total injected amount
2005-09-16	I-131	<6E-04
2005-09-20	I-131	<2E-03
2005-09-26	I-131	<1E-03
2005-10-12	I-131	<3E-02

The on-line measurement of the guard loop showed a decreasing value with time during the experiment which first was believed to be caused by an equilibration of the radon content of the guard section. However, the probe finally stopped giving any pulse output, so the results of the guard measurement may have been affected by a slow degradation of the probe function.

Pilot borehole (KA3065A02:3)

The pilot borehole groundwater sample of 2005-11-24 showed no content of ^{131}I , which was an expected result since no tracers were found in the first guard section either and the pilot borehole is further away with a larger dilution in case of a leakage.

Dose rate measurements at fence and in container 1

The dose rates at the fence and in container 1 were stable and slightly lower than $0.2 \mu\text{Sv/h}$ during the test period. The contents of gamma-emitting radionuclides in the stock solutions were quite low, about 3 MBq, which is why no significant increases in dose rates were obtained during this experiment.

3.9 Other equipment tests

3.9.1 PLC/InTouch control and monitoring unit

The tests of the input and output channels showed that all channels except the oxygen monitor in container 1 worked properly. A few channel cross couplings were discovered and corrected during the test.

3.9.2 Power Supply

During a planned interrupt in the power supply to the LTDE test site for change of power support, the UPS functions were monitored. The UPS units lasted for a minimum of 30 minutes. This time is shorter than the system was originally designed for (~2h), but good enough in the new situation where the diesel backup generator should result in a power interrupt of about 10 to 20 s.

However, it was noted that some equipment is not supplied by the UPS units. The level indicators and the RNI-instruments are supplied by DC-voltage without UPS backup. Therefore the RNI-instruments needs to be restarted even after a short power interrupt. Some other units also need to be restarted in the event of a power interrupt to LTDE. The HPGe-detector also needs to be restarted since it has a non-UPS backed up power supply. The reason for this is that the power from the UPS-units causes disturbances in the HPGe-detection system, possibly from ground loops. The units that need to be restarted are shown in Table 8.

The alarm will also be triggered from the level indicators and the RNI-instruments during the start-up of the diesel aggregate. However, the alarms cause automatic functions in the PLC/InTouch to disconnect other equipment (e.g. the pressure regulator and the circulation pump are switched off). When power returns the alarms disappear, but some of the switched off equipment needs to be manually restarted.

It is desired to install UPS-backed up power supply to the level indicators and the RNI-instruments prior to a long time experiment. Further, voltage monitoring after both earth faults breakers is desirable. It may also be beneficial to install auxiliary contacts on the fuses in the distribution boxes. Further, the automatic functions should be invented and adjusted prior to a start of a long term experiment.

Table 8. Equipment that need to be manually restarted after a power interruption at LTDE.

RNI-instruments

HPGe-detector

Circulation pumps (test section, guard section, pilot borehole section)

Pressure regulator

3.9.3 Alarm system

The alarms were coupled to the alpha system and tested with positive results 2005-09-08. Furthermore, alarms have been triggered during the test period by testing of the diesel backup generator (2005-09-22), communication loss with the LTDE2 computer (2005-11-26) and by work (sampling etc) in the circulation system without prior blocking of alarm groups (2005-11-24). The control room at Clab have had access to the LTDE/TRUE-completion on-call duty list and alarm instructions supplied by the project.

3.9.4 Circulation equipment tightness test

A continuous small drift in the position of the pressure regulating piston was observed in the beginning of October. The drift was about 0.4 mm per day, thus indicating a leakage of about 300 µl per day. Visual inspections of valves and fittings in the inert gas boxes have not revealed the source of the leakage. The relatively high temperature and dry nitrogen atmosphere leads to a fast evaporation of possible droplets. Salt depositions have not either been observed, which could indicate the leakage position.

A test was performed to confirm that the leakage is within the circulation equipment in container 1. The valves to the borehole were closed and a re-coupling of the pressure transmitter was done in order to measure the pressure in the circulation equipment that was now isolated from the borehole. The system outside of the borehole was pressurised to 3470 kPa. 44 h later the pressure had decreased to 2890 kPa which indicated a leak in the valves, fittings or equipment. In the next step, the pressure regulator was started and the piston position was monitored. Again a drift of about 0.4 mm per day was observed. Consequently, the small leak is probably within the equipment in container 1. Further search to find the leakage should be done by repeating the pressure test for the different parts of the equipment.

3.10 Other observations

The temperature in the experiment container (container 1) has been high, about 30 to 32° C during the test period. The temperature within the inert gas boxes were 2 to 5 degrees lower due to the electrical coolers. The container is insulated and the mechanical ventilation is not sufficient to cool the heat generated by the equipment inside the container. It is recommended to take measures in order to maintain a temperature of about 20° C in the container.

4 Conclusions

The functionality test with short-lived radionuclides showed that concentration-time curves based on sampling and on-line measurements of the radioactivity in the test section can be produced with the present experimental set-up. The successively decreasing concentrations with time for the sorbing tracers show that sorption processes in the test section can be studied at the LTDE site. Only a minor sorption on tubing could be measured for the most strongly sorbing tracer which indicates that the sorption occurs to a major extent on the stub and slimhole rock surfaces. It is concluded that sampling and on-line measurements complement each other and that both should be done in future experiments.

Observation of the relative concentrations at 2 weeks experimental time show an increase in sorption strength in the order $\text{Ca(II)} \leq \text{I(-I)} < \text{Np(V)} < \text{Cd(II)} < \text{Cs(I)} < \text{Lu(III)} < \text{Hf(IV)}$. The trend generally follows the charge of the major species of the sorbing complexes. Ca, with its strong hydration shell, is non-sorbing in the relatively saline water and a weak sorption of iodine species is observed. The reason for the weak sorption of iodine is not clear. Speciation calculations for Cd, Lu, Np and Hf give a consistent picture of the observed concentration decreases in relation to the dominating species for the different elements. Cs was relatively strongly sorbing in accordance with earlier field tests at Äspö.

The experimental conditions were stable according to monitoring of pressure and pH, apart from short pressure disturbances due to sampling and injection. The pressure regulator worked well. The NW-2, NW-3 and related structures are of vital importance for the hydraulic pressure responses in the LTDE boreholes. Pumping, drilling etc should not be performed in these structures during the forthcoming long term experiment.

The redox potential was slowly decreasing during the experiment, but still positive. Thus, low negative redox potentials have not been obtained in the test section during the test period with nitrogen flushing of the inert gas boxes. The redox potentials in the test section may be affected by mineral oxidations that occurred during the time that the borehole was open prior to the borehole installations. Consequently, more circulation time with a closed system may be needed to obtain reducing conditions.

The tracer production, injection and sampling procedures that were developed were functional and more than 95% of the tracers in the stock solutions were injected. About 2 weeks of circulation time were needed to obtain good mixing (constant concentration) for the inert and weakly sorbing tracers. The slow mixing is likely caused by the existence of zones of relatively stagnant groundwater within the circulation system such as in front of the stub surface and in the pressure regulator cylinder. The mixing behaviour in the test section is of minor importance for a sorption-diffusion test that will last for several months or more. However, the use of the KA3065A03 borehole for short term tests (hours to days) is not recommended since the slow mixing complicates the evaluation in such a case.

The equipment tests show that the systems generally worked as expected. Some modifications are proposed to be done regarding automatic alarm functions and complementary electrical control in the system. Rearrangement of the placement of the electrochemical flow cell in the glove box is also proposed in order to improve the practical work in the glove box and to reduce disturbances in the measurements. Furthermore, the experiment container needs cooling in order to reduce the temperature from 30 to 20 degrees C. No tracers were detected in the guard section which indicates that the test section is tight towards the guard section.

5 Future perspectives for a long term diffusion experiment

A summary is given below of some points that should be considered in the planning of a long term diffusion experiment regarding experimental and technical conditions at the LTDE site. The actions should be planned with consideration of the duration of a future experiment:

- Experimental conditions
 - *Redox potential*: Since it has not yet been demonstrated that very low redox potentials may be reached at LTDE it is also unclear whether redox-sensitive tracers can be obtained in their reduced forms in a future experiment. However, the strong interactions of +IV metals with surfaces may affect the actual redox potential at which the reduced form is obtained. We therefore recommend that scoping calculations addressing sorption reactions are done for +IV elements for the present experimental conditions. The results can then be a base for decision of tracer selection in a future experiment at the site. We also recommend that circulation of the test section with redox monitoring and nitrogen flushing of the inert gas boxes are continued to allow for maximum decrease in redox potential.
 - *Non-sorbing tracers*: Iodine showed a weak sorption with time in the functionality test and is therefore not a preferred tracer in a future experiment. The selection of an inert tracer that can be analysed in the rock material after at least a year excludes some often used inert tracers. Tritiated water cannot be used for rock analysis due to evaporation during handling; bromide tracers are too short-lived; color dye tracers and metal-complexes are undesired due to risk of complexation of the other metal tracers with high charges. Thus, ^{36}Cl is the only reasonable choice, although it requires chemical separation procedures since it has no γ -emission that can be measured using γ -spectrometry.
 - *Experiment time*: A minimum experiment time of 2 two 3 months is recommended with the regards to the mixing time.
- Technical conditions
 - *High temperature in container 1*: Increased cooling of container 1 is required in order to decrease the temperature to about 20 degrees C.
 - *Electrochemical flow cell*: The flow cell position should be changed for practical reasons and in order to decrease disturbances from glove box work. Further reduction of possible electrical/magnetic disturbances may be considered.

- *Equipment maintenance:* A maintenance plan should be produced for moving parts in the system such as the circulation pump, piston o-rings in the pressure regulator etc. Necessary maintenance should preferentially be done before or after experiment phases.
- *PLC automatic security functions:* The automatic security functions in the PLC/InTouch should be invented and adjusted after consideration.
- *Electrical power supplies:* It is recommended to install UPS backup for level indicators, RNI-instruments and to re-establish UPS-backup for the HPGe detector or install a separate UPS for the HPGe. It should be considered to install voltage monitoring after earth fault breakers and auxiliary contacts on the fuses in the distribution boxes.

References

Allison, J.D., Brown, D.S., and Novo-Gradac, K.J., 1990. MINTEQA2/PRODEFA2-- A geochemical assessment model for environmental systems--version 3.0 user's manual: Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia, 106 p.

Andersson, P., Byegård, J., Nordqvist, R. and Wass, E., 2005. TRUE Block Scale continuation project. BS2B tracer tests with sorbing tracers. Swedish Nuclear Fuel and Waste Management Company, SKB IPR-05-01.

Behrens, H. New insights into the chemical behaviour of radioiodine in aquatic environments, in Proc. "Environmental migration of long-lived radionuclides" IAEA, Wien, 1982

Byegård, J., Johansson, H., Andersson, P., Hansson, K. and Winberg, A., 1999. Test Plan for the Long-Term Diffusion Experiment. Swedish Nuclear Fuel and Waste Management Company, SKB IPR-99-36.

Byegård J., Ramebäck, H. and Widestrand, H., 2002. TRUE-1 Continuation project. Use of radon concentrations for estimation of fracture apertures – Part 1: Some method developments, preliminary measurements and laboratory experiments. Swedish Nuclear Fuel and Waste Management Company, SKB IPR-02-68.

Byegård, J., Nordqvist, R. and Widestrand, H., 2004. Investigation of the possibility of using single-well in situ-sorption measurements of retention parameters in the site investigations. Swedish Nuclear Fuel and Waste Management Company, SKB PIR 04-16.

Byegård, J. and Tullborg, E.-L., 2006. TRUE BS Continuation, batch sorption experiments on rim zone material, report in progress. Swedish Nuclear Fuel and Waste Management Company

Carbol, P. and Engkvist, I., 1997. Compilation of radionuclide sorption coefficients for performance assessment. Swedish Nuclear Fuel and Waste Management Company, SKB R-97-13.

Charlton, S.R. and Parkhurst, D.L., 2002. PhreeqcI--A graphical user interface to the geochemical model PHREEQC: U.S. Geological Survey Fact Sheet FS-031-02, 2 p.

LLNL, 2005. llnl.dat 2005-02-02, Data are from 'thermo.com.V8.R6.230' prepared by Jim Johnson at Lawrence Livermore National Laboratory, in Geochemist's Workbench format. Converted to Phreeqc format by Greg Anderson with help from David Parkhurst. A few organic species have been omitted. Delta H of reaction calculated from Delta H of formations given in thermo.com.V8.R6.230 (8 Mar 2000).

Parkhurst, D.L. and Appelo, C.A.J., 1999. User's guide to PHREEQC (Version2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 310 p.

Pedersen, K., 2005. Analys av förekomst av bakterier i LTDE, 2005-09-21. Microbial Analytics Sweden AB.

Pehkonen, J., 2005a. Tryckkompenserad glaselektrod. Swedish Nuclear Fuel and Waste Management Company, internal document SKB MD 433.YYYY-01, (in progress).

Pehkonen, J., 2005bYYYY, Tryckkompenserad referenselektrod. Swedish Nuclear Fuel and Waste Management Company, internal document SKB MD 433.YYYY-01, (in progress).

Vilks, P., 2004. Review: Long Term Diffusion Experiment.. Swedish Nuclear Fuel and Waste Management Company, internal document.

Vilks, P., Miller, N., H., 2005. Status report on 2004 supporting work for SKB's long term diffusion experiment. Report No: 06819-REP-01300-10098-R00. Nuclear Waste Management, Ontario Power Generation.

Wacker P., Berg C. and Bergelin A., 2004. Oskarshamn site investigation. Complete hydrochemical characterisation in KSH01A. Swedish Nuclear Fuel and Waste Management Company, SKB P-04-12.

Wass, E., 2005. Long Term Diffusion Experiment (LTDE). Hydraulic conditions of the LTDE experimental volume – results from Pre-tests 0.1 – 6. Swedish Nuclear Fuel and Waste Management Company, SKB IPR-05-25.

Widestrand, H., Andersson, P., Byegård, J., Skarnemark, G., Skålberg, M. and Wass, E., 2001. In situ migration experiments at Äspö Hard Rock Laboratory, Sweden: results of radioactive tracer migration studies in a single fracture. Journal of Radioanalytical and Nuclear Chemistry 250(3), 501-517,

Widestrand, H. and Byegård, J., 2005. Teknisk beskrivning av fältexperiment med radioaktiva spårämnen i Äspölaboratoriet. LTDE – funktionalitetstester med kortlivade radionuklider 2005. Swedish Nuclear Fuel and Waste Management Company, internal document (in swedish).

Winberg, A., Hermanson, J., Tullborg, E.L. and Staub, I., 2003. Long-Term Diffusion Experiment. Structural model of the LTDE site and detailed description of the characteristics of the experimental volume including target structure and intact rock. Swedish Nuclear Fuel and Waste Management Company, SKB IPR-03-51.

Yoshida, Y. and Shibata, M., 1999. Establishment of Data Base Files of Thermodynamic Data developed by OECD/NEA. Part II – Thermodynamic data of Tc, U, Np, Pu and Am with auxiliary species. JNC Technical Report, JNC TN8400 2004-025 (2004, in Japanese). Waste Isolation Research Division, Waste Management and Fuel Cycle Research Center, Japan Nuclear Cycle Development Institute (JNC), Database Version : 011213c2.tdb. *Reference thermodynamic data (except for Technetium): M.Yui, et al. JNC Thermodynamic Database for Performance Assessment of High-level Radioactive Waste Disposal System. JNC Technical Report, JNC TN 8400 99-070. For Technetium: Rard, J.A., et al., 1999, Chemical Thermodynamics of Technetium, OECD Nuclear Energy Agency, Amsterdam North - Holland*

APPENDIX A: Separation and measurement of the ^{131}Cs tracer

Introduction

The ^{131}Cs tracer offers some promising properties for use in in-situ experiments. It has a comparatively short half-life (9.69 days) which makes it advantageous in this type of experiment where one wants the tracer to have decayed within some months. The tracer can also be produced with very high specific activity which allows uses in very high radioactive content without any particular increase of the chemical concentration. The major disadvantage is that the tracer lacks measurable γ -radiation which makes the tracer somewhat more difficult to detect and quantify.

Production

The ^{131}Cs tracer used in this functionality test was produced by neutron irradiation (5 days) of 2.25g $\text{BaCO}_3(\text{s})$ (99.999% purity, Aldrich) at IFE, Norway. Approximate neutron flux was estimated to $1\text{E}13 \text{ n/s/cm}^2$. The production occurs by neutron capture of the stable isotope Ba-130 (0.106% of natural Ba) which then forms Ba-131 which decays with a half life of 11.5 d to ^{131}Cs . The cross section for neutron capture of Ba-130 is 5.5 b.

The ^{131}Cs tracer was separated from the batch approximately 4 days after the neutron irradiation was finished. Based on calculation using the mentioned values, in some cases rather uncertain, an amount of 36 MBq should thus be present at the injection time for the in situ experiment.

Preparation

The irradiated $\text{BaCO}_3(\text{s})$ was dissolved in 25 ml concentrated HCl. Thereafter, Na_2SO_4 was added to the solution to obtain a 10% excess of SO_4^{2-} vs Ba^{2+} . The formed precipitation was allowed to undergo sedimentation, thereafter as much solution as possible was extracted by a syringe and passed through a 20 nm filter. To investigate the presence of any impurities in the solution, the extracted solution was measured by γ -spectrometry. The γ -spectrum and the corresponding activities of impurity isotopes in the solution are given in Figure A-1 and Table A-1 respectively.

An interesting observation is that only 160 Bq of Ba-131 is measured in the stock solution. Based on calculations of the produced amount of 52 MBq, it is estimated that >99.9998% of the Ba is precipitated by the sulphate precipitation. This indicates a total chemical concentration of Ba in the stock solution $\sim 100 \mu\text{g/l}$.

Table A-1. Isotopes identified by γ -spectrometry in the ^{131}Cs stock solution.

Identified isotope	$t_{1/2}$ (d)	Activity ^{A)} (Bq)	Possible production reactions
<i>Isotopes obtained by irradiation of Ba</i>			
Ba-131	11.5	160	$^{130}\text{Ba}(n,\gamma) \rightarrow ^{131}\text{Ba}$
Cs-129	1.33	60	$^{130}\text{Ba}(n,\gamma) \rightarrow ^{129}\text{Ba}(\text{decay}) \rightarrow ^{129}\text{Cs}$
Cs-132	6.47	2000	$^{132}\text{Ba}(n,p) \rightarrow ^{132}\text{Cs}$
Cs-136	13.16	50	$^{136}\text{Ba}(n,p) \rightarrow ^{136}\text{Cs}$
La-140	1.68	200	$^{138}\text{Ba}(n,\gamma) \rightarrow ^{139}\text{Ba}(\text{decay}) \rightarrow ^{139}\text{La}(n,\gamma) \rightarrow ^{140}\text{La}$ (and/or fission of impurities of ^{235}U)
<i>Isotopes obtained by irradiation of impurities in the BaCO_3</i>			
Na-24	0.623	4000	$^{23}\text{Na}(n,\gamma) \rightarrow ^{24}\text{Na}$
K-42	0.515	100	$^{41}\text{K}(n,\gamma) \rightarrow ^{42}\text{K}$
As-76	1.1	300	$^{75}\text{As}(n,\gamma) \rightarrow ^{76}\text{As}$
Br-82	1.47	200	$^{81}\text{Br}(n,\gamma) \rightarrow ^{82}\text{Br}$
I-131	8.02	50	fission of impurities of ^{235}U (?)
Lu-177	6.71	400	$^{176}\text{Lu}(n,\gamma) \rightarrow ^{177}\text{Lu}$
Au-198	2.69	200	$^{197}\text{Au}(n,\gamma) \rightarrow ^{198}\text{Au}$

A) Refers to the activity at the time for the injection, i.e., ~4 days after the end of the irradiation

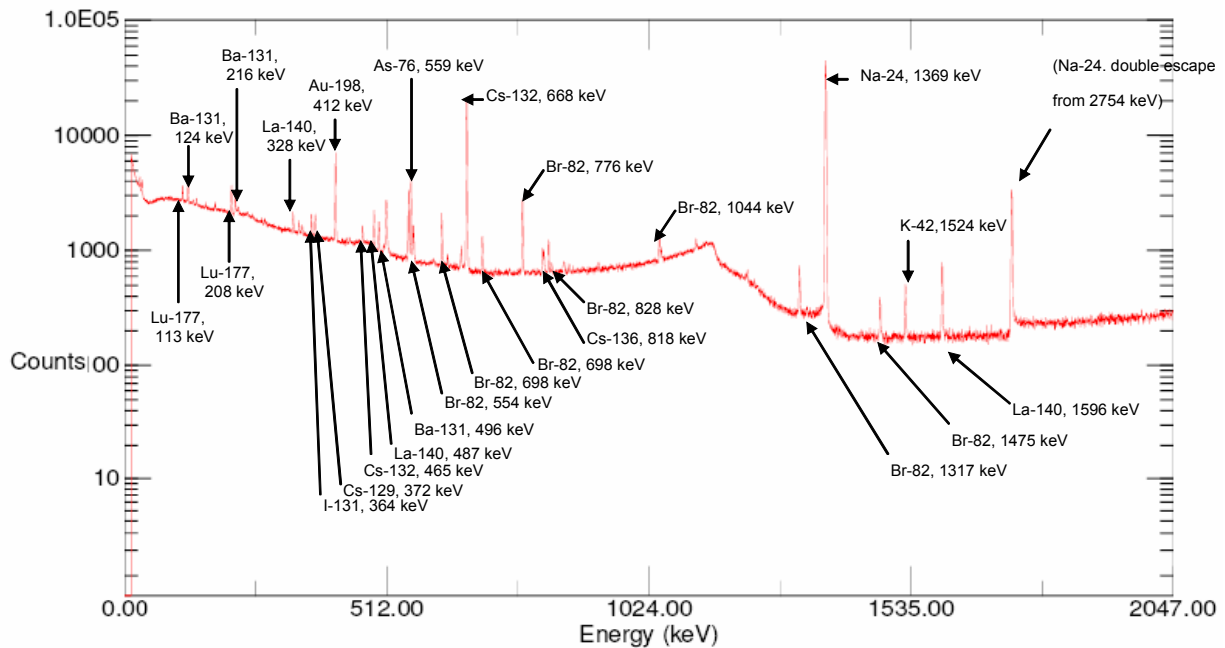


Figure A-1. Spectrum for the γ -spectrometry measurement of the ^{131}Cs stock solution.

Sample measurement

Since the decay of ^{131}Cs is not associated with any measurable γ -radiation, the much less selective liquid scintillation counting technique has to be applied for the measurement. Since a cocktail of radionuclides were used in this experiment, interferences from other radionuclides should be expected for a simple sample measurement using liquid scintillation technique. Therefore, a selective Cs separation is advantageous for a correct quantification of ^{131}Cs .

In this experiment, the following procedure for separation and measurement of ^{131}Cs was applied. A chemical separation procedure was used in which 1 ml sample was mixed with 9 ml 0,01M HCl followed by an addition of 10 mg of ammonium phosphomolybdate hydrate (Aldrich). This compound is known to be a very strong Cs-trapper, cf. e.g. Byegård 2002. This mixture was thoroughly mixed and allowed to equilibrate for 1 hour and thereafter the slurry was passed through a 20 nm syringe filter. After that, 1 ml of 1M NaOH was passed through the filter (to dissolve the Ammonium phosphomolybdate hydrate) and the solution was collected in a 20 ml plastic scintillation tube. 15 ml of scintillation cocktail (Emulsifier Safe, Perkin Elmer) were added and measurement was performed using a Wallac 1414 Guardian.

In order to estimate the efficiency of the separation procedure, a comparative measurement was performed for an ammonium phosphomolybdate hydrate treated sample and an equivalent sample spiked, without any treatment, into a scintillation cocktail. The spectrum obtained from the different measurements together with the graphs showing the decrease in counting rate versus time are presented in Figure A-2 (treated sample) and Figure A-3 (non-treated sample). As expected for the treated sample, the decrease in counting rate can almost perfectly be explained from the tabulated half-life of ^{131}Cs , i.e. 9.69d. However, for the case of the non-treated sample, a systematic deviation of the measured and projected values can be seen, which probably can be explained by interferences of other (and more long-lived) radionuclides. It can be observed that the deviation is most severe when including the high energy part of the spectrum.

Comparing the count rate in the low energy part of the spectrum (i.e., channel # 1-180) from the treated and non-treated sample, it can be estimated that the efficiency of the separation process is >90%. Possible causes for obtaining this apparent non-quantitative separation process are:

- Non-quantitative adsorption of Cs on the ammonium phosphomolybdate (caused by e.g., the presence of Cs in a colloidal phase in the groundwater sample).
- Non-quantitative dissolution of the ammonium phosphomolybdate in the NaOH treatment
- Adsorption of Cs in the syringe filter after the dissolution
- Quenching caused by the dissolved ammonium phosphomolybdate giving a decreased counting rate.

Based on the observed background counting rate, an estimation of the detection limit (Currie 1968) to 50 Bq per liter can be done by application of this method. However, a quantitative extraction of Cs from a one litre solution to a syringe filter was shown by Byegård 2002. Consequently, if one litre samples are available, the detection limit should be possible to decrease to ~50 mBq per litre.

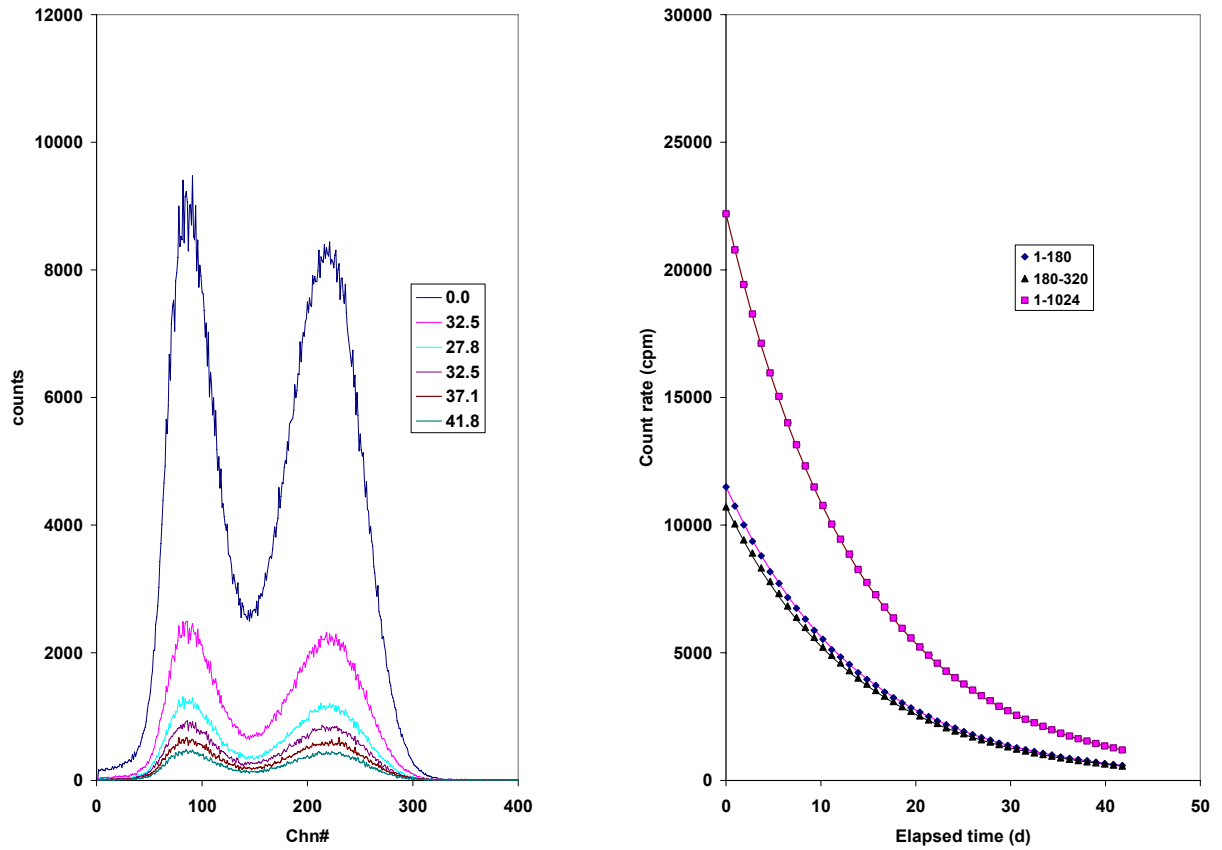


Figure A-2. Liquid scintillation spectrum (left) for sample #5 (treated with ammonium molybdenum phosphate). Results are given for a number of different times (days) after the preparation of the liquid scintillation sample. To the right, the decrease of counting rate versus the elapsed time is presented. The dots represents the measured value and the line shows the projected decrease of the counting rate, based on the tabulated half-life of ^{131}Cs (9.69 d)

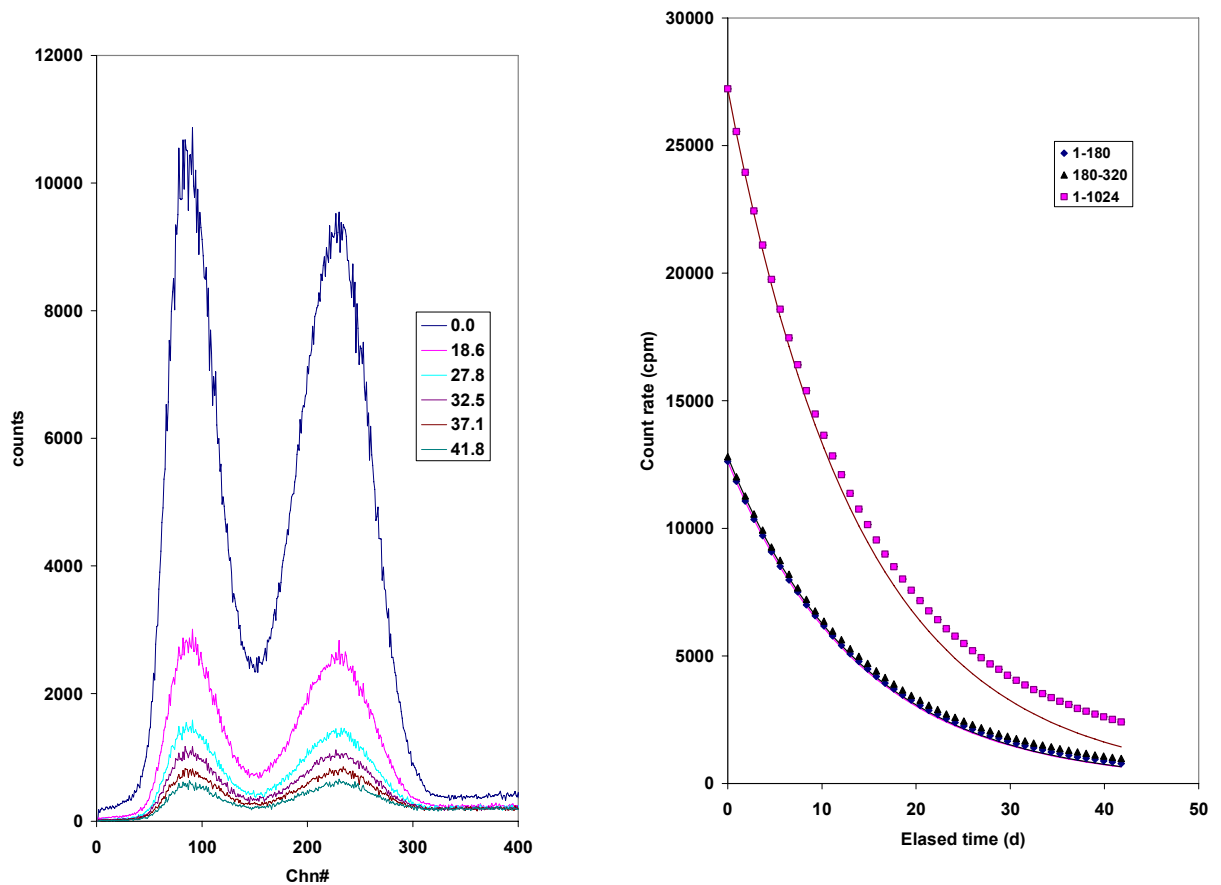


Figure A-3. Liquid scintillation spectrum (left) for sample #5, without treatment with ammonium molybdenum phosphate. Results are given for a number of different times (days) after the preparation of the liquid scintillation sample. To the right, the decrease of counting rate versus the elapsed time is presented. The dots represents the measured value and the line shows the projected decrease of the counting rate, based on the tabulated half-life of ^{131}Cs (9.69 d)

References

Byegård, 2002. Tracer Retention Understanding Experiments – Continued sampling and tracer measurement in the TRUE-1 experiment and the TRUE Block Scale experiment, phase C. SKB IPR-02-69, Swedish nuclear fuel and waste management company, Stockholm.

Currie, 1968. Limits for qualitative detection and quantitative determination: Application to radiochemistry, *Anal. Chem.* 40, 586-593 (1968).

APPENDIX B: Detailed description of injection and sampling

1. Injection procedure

Transfer of stock solution to tubing loop

The length of each loop was adjusted to, in addition to the stock solution, hold approximately 6-7 ml guard water. The purpose of having guard water in the beginning and in the end of each loop was to minimize the loss of tracer solution at the transfer of the stock solution from the glass vessel to the tubing loop.

The two loops were joined to injection valve 14 and 15, respectively, at ports 1 and 4, see Fig. 4 and B-1. The injection valves 14 and 15 were placed in series, 14 before 15. The injection loop joined to valve 14 comprised the alkaline stock solution while the acidic stock solution was joined to valve 15. In the following, the procedure to load the injection loop joined to valve 15 is outlined. The same is valid for loading of the injection loop joined to valve 14.

A syringe was joined to port 2 and a short tube was joined to port 3 of the injection valves. The tube had a length sufficient to reach down to the bottom of the glass vessel containing the stock solution. When the injection valve is in its "LOAD" position, ports 1 and 2 are connected as well as ports 3 and 4. This makes it possible, with the help of the syringe, to suck an aqueous solution, guard water or stock solution, into the loop. The tubing loop was filled in three steps as follows (see also Figure B-1):

- 1) As a first step the short tube was immersed in a beaker with guard water. Approximately 3-4 ml was sucked into the syringe-injection loop-tube set-up.
- 2) Next, the tube was transferred to the glass vessel and immersed in the stock solution. The vessel was tilted to ensure that almost all of the stock solution was sucked into the tubing loop.
- 3) When almost all of the stock solution was sucked into the set-up, a small amount of guard water was added to the vessel. Suction with the syringe continued until small droplets of water could be seen in the inlet of the syringe, indicating the syringe-injection loop-tube set-up was filled with solution. Thereafter, the shut-off valves were closed.

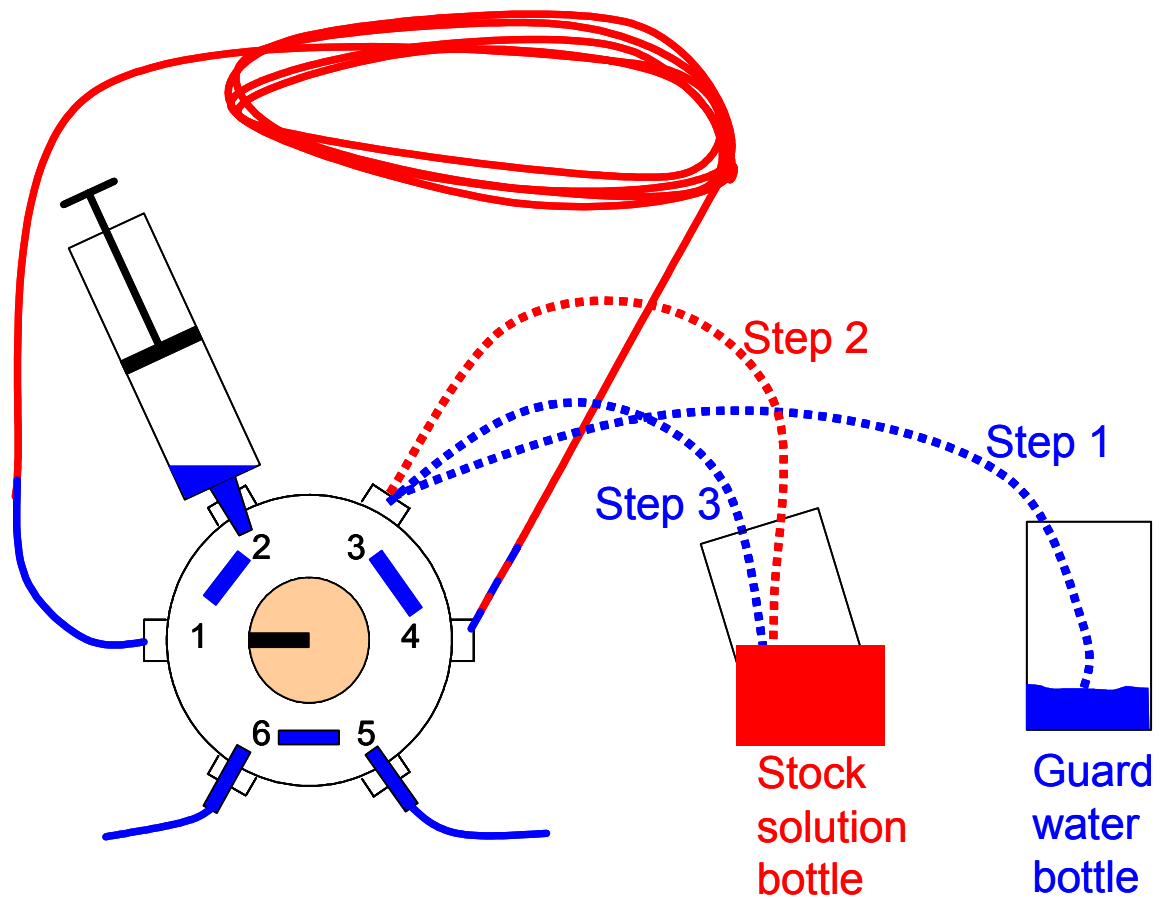


Figure B-1. Drawing of equipment set-up for controlled transfer of the stock solution to the injection loop. The three steps of filling the loop are described in the text above.

Thus, the stock solution was now transferred to the injection loop, ready to be connected to the circulation equipment. The only residual of the stock solutions were left in the vessels, and could easily be returned to Baslab and be sampled and measured to determine the non-injected amount of radioactivity

Injection

The injection was done by switching the valve to the “INJECTION” position, connecting ports 1 and 6 as well as ports 4 and 5. The stock solution in the injection loop was then transferred into the circulation loop as a plug flow pulse. It was desired that a plug flow within the tubing should be obtained until the stock solutions would reach the experimental test section, in which mixing would occur and the two solutions would be pH-equilibrated. A photo of the equipment set-up is shown in Figure B-2.

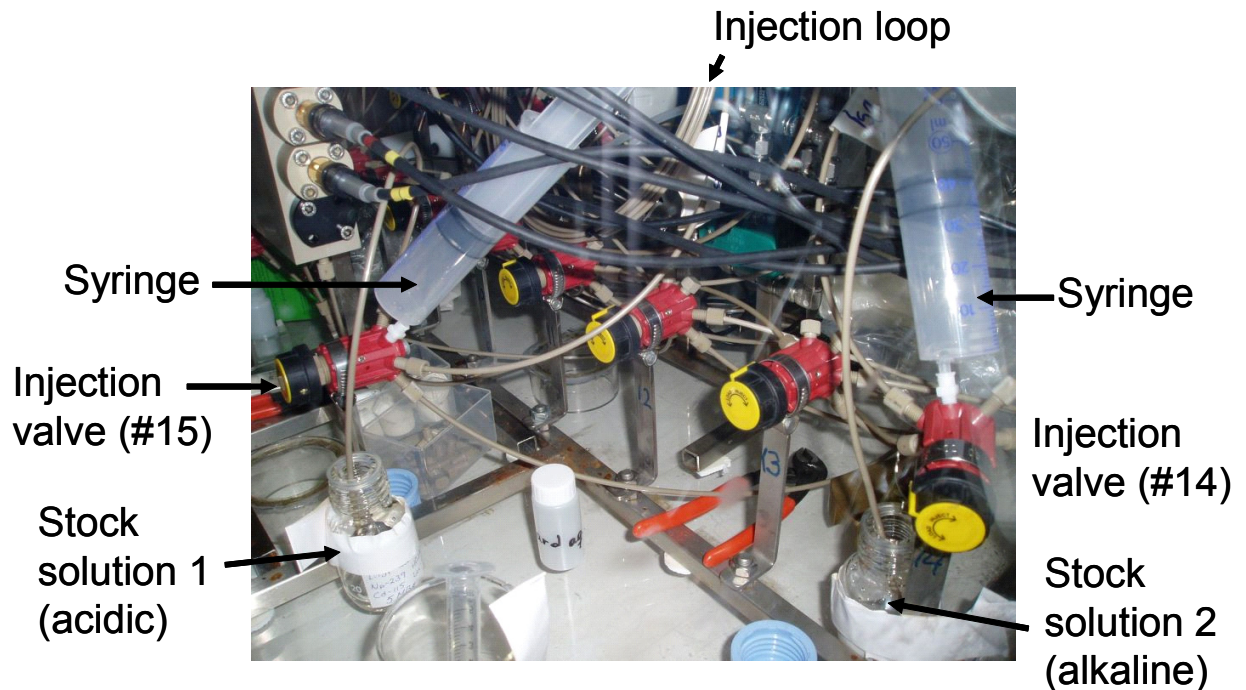


Figure B-2. Injection valves photograph with tubes to stock solution bottles, syringes and one injection loop visible behind the left syringe.

2. Sampling procedure

A short tube was connected to the outlet of the needle valve aimed to facilitate sampling in 20 ml plastic vials (scintillation vials).

A description of the sampling procedure is outlined below.

1. The circulation in the test section was shut down.
2. A scintillation vial was placed under the tube.
3. Valve 9 was switched into the “INJECT” position.
4. The needle valve was opened with precaution. A pressure drop less than 2-3 bar was desirable.
5. The valve 9 was switched to “LOAD” position when approximately 12-15 ml had been withdrawn from the test section.

Thereafter the needle valve was set to fully open allowing remaining solution to drop into the sample. To ensure that no solution will be left in the sampling equipment after each sampling a syringe was joined to port 2 on valve 9 and nitrogen was pressed, with the aid of the syringe, through port 2 and 1 to flush the needle valve and the tube.

Filtered samples

In order to be able to take filtered water samples the tube was replaced by a filter. To the filter a syringe was joined which was arranged to fit into a scintillation vial. The same sampling procedure as outlined above was used.

APPENDIX C: One-dimensional diffusion model (slightly modified version of SKB PIR-04-16)

A conceptual model for the transformation of a radial diffusion case into a simplified one-dimensional case is described in Figure C-1.

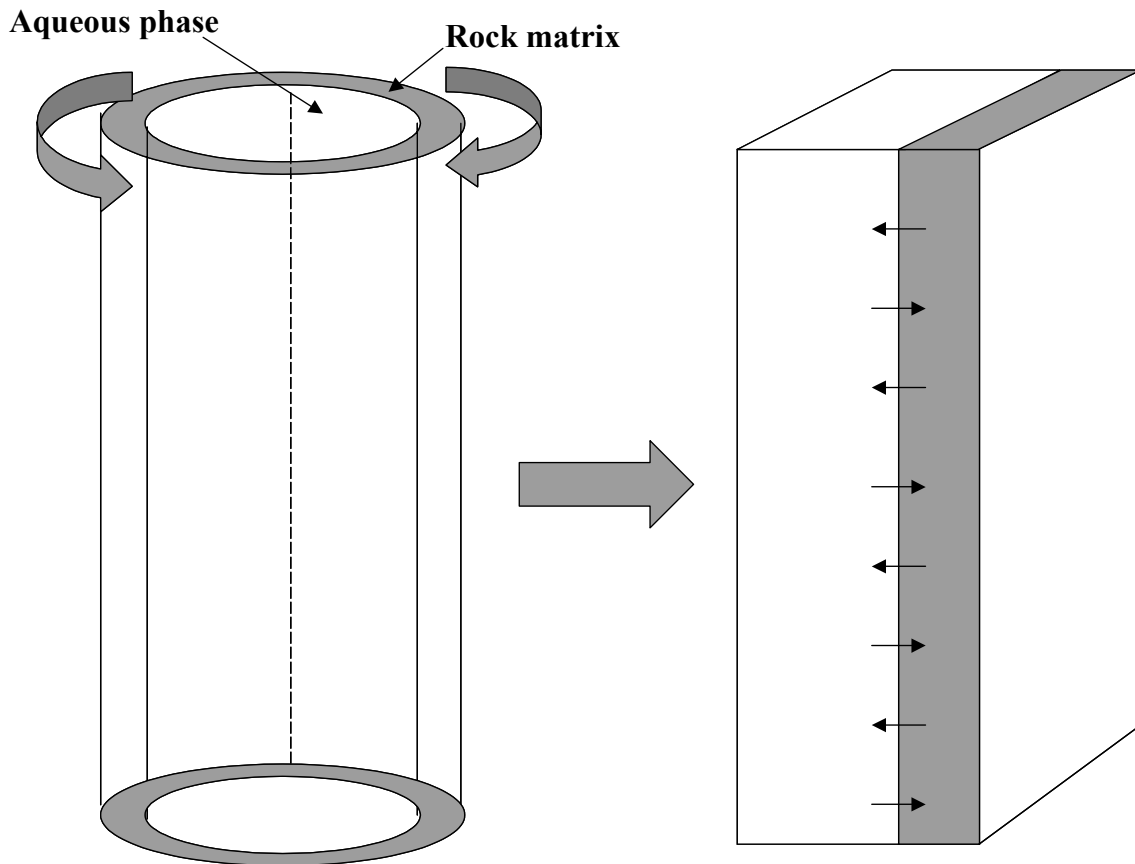


Figure C-1. Conceptual model for the interpretation of a radial diffusion case into a one-dimensional diffusion case.

The general one dimensional diffusion equation is expressed by;

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

In the present situation the interaction can be regarded as diffusion from a stirred solution of limited volume into a plane sheet. In order to benefit from the analytical solution of this case given by Crank (1975), a case where diffusion from both sides of the sheet occurs will be considered. The sheet occupies the space $-l \leq x \leq l$, while the solution is of limited extent and occupies the spaces $-l-a \leq x \leq -l$ and $l \leq x \leq l+a$. The occupation length of the water phase (a) is set to:

$$a = V / A + K_a \quad (2)$$

where V corresponds to the total volume used in the borehole experiment (i.e., both the volume in the borehole section and the volume of the circulation equipment) and A is the sum of the stub surface area and borehole wall area.

The length of the sheet (l) has no influence of the rate of the loss of tracer in the water phase as long as the contribution of tracer diffusing from one side to the other can therefore be neglected. The length can therefore be set arbitrarily and in this particular case l has been set in order to obtain a tracer concentration in the middle of the sheet ($x=0$) that is at least 10^{10} times lower than the tracer concentration in surface layer of the sheet (i.e., $x=l$ or $x=-l$)

The concentration of the solute in the solution is always uniform and is initially C_0 , while the sheet initially is free from solute. The following boundary conditions therefore apply:

$$C=0, \quad \alpha_r \frac{\partial C}{\partial t} = \pm D \frac{\partial C}{\partial x} \quad -l \leq x \leq l, \quad t = 0 \quad (3)$$

and

$$\alpha_r \frac{\partial C}{\partial t} = \pm D \frac{\partial C}{\partial x}, \quad x = \pm l, \quad t > 0 \quad (4)$$

The analytical solution to this problem has been given by Crank (1975). The total concentration within the sheet, C_x , (including both the pore water concentration and the mass sorbed on the rock) at the distance x at a given diffusion time of t is given by the expression:

$$C_x = C_\infty \left\{ 1 + \sum_{j=1}^{\infty} \frac{2(1 + \alpha_r) \exp\left(-\frac{D_a q_j^2 t}{l^2}\right) \cos\left(\frac{q_j x}{l}\right)}{1 + \alpha_r + \alpha_r^2 q_j^2} \frac{1}{\cos q_j} \right\} \quad (5)$$

where C_∞ is the concentration in the sheet after infinite time and the q_j values are the non-zero positive roots of:

$$\tan q_j = -\alpha_r q_j \quad (6)$$

and α_r is the ratio of the capacities of the rock and water phase, defined as;

$$\alpha_r = \frac{a}{l(\varepsilon + K_d \rho)} \quad (7)$$

Furthermore, the decrease of the concentration of tracer in the start cell, C_1 , can be calculated according to:

$$C_1 = C_{1(0)} - \frac{C_\infty m}{V_1 \rho} \left\{ 1 - \sum_{j=1}^{\infty} \frac{2\alpha_r (1 + \alpha_r) \exp\left(\frac{-D_a q_j^2 t}{l^2}\right)}{1 + \alpha_r + \alpha_r^2 q_j^2} \right\} \quad (8)$$

where $C_{1(0)}$ corresponds to the initial concentration in the start cell.

By applying mass balance, C_∞ can be calculated according to:

$$C_\infty = \frac{C_0 a}{l + a/(\varepsilon + K_d \rho)} \quad (9)$$

However, for the present functionality test, the concentration profile within the rock will not be possible to measure. Instead, the decrease of the concentration in the water phase (caused by diffusion and/or sorption in the rock) will be the only available experimental parameter that can be measured. The analytical solution for calculating the total amount of tracer in the sheet (M_t) after a given experimental time (t) is expressed as:

$$\frac{M_t}{M_\infty} = 1 - \left\{ \sum_{j=1}^{\infty} \frac{2\alpha_r(1+\alpha_r)}{1+\alpha_r+\alpha_r^2 q_j^2} \exp\left(\frac{-D_a q_j^2 t}{l^2}\right) \right\} \quad (10)$$

where M_∞ corresponds to the total amount of tracer in the sheet after infinite experimental time. Applying mass balance, M_∞ can be expressed as:

$$M_\infty = \frac{2aC_0}{1+\alpha_r} \quad (11)$$

where C_0 is the initial concentration of tracer in the water phase. Furthermore, M_t can be expressed as:

$$M_t = (M_0 - M_{aq(t)}) = a(C_0 - C_{aq(t)}) \quad (12)$$

where M_0 is the initial amount of tracer added to the system, $M_{aq(t)}$ is the amount of tracer in the water phase after an experimental time of t and $C_{aq(t)}$ is the corresponding concentration of tracer in the water phase.

By inserting (11) and (12) into (10) and by rearranging, the following expression is obtained:

$$\frac{C_{aq(t)}}{C_0} = 1 - \left\{ \frac{1}{1+\alpha_r} - \sum_{j=1}^{\infty} \frac{2\alpha_r}{1+\alpha_r+\alpha_r^2 q_j^2} \exp\left(\frac{-D_a q_j^2 t}{l^2}\right) \right\} \quad (13)$$

References

Crank, J., 1975. The mathematics of diffusion, 2nd edition, Oxford Univ. press, London.

APPENDIX D: Chemical analysis of KA3065A03:1 sample 2005-09-15

ELEMENT	SAMPLE	KA3065A03:1 2005-09-15 LTDE Test sect
Ca	mg/l	1870
Fe	mg/l	<0.004
K	mg/l	10,9
Mg	mg/l	45,9
Na	mg/l	1900
S	mg/l	130
Si	mg/l	5,71
Al	µg/l	11,2
Ba	µg/l	92,3
Cd	µg/l	0,2
Co	µg/l	<0.05
Cr	µg/l	0,427
Cu	µg/l	2,98
Li	µg/l	1330
Mn	µg/l	59,4
Mo	µg/l	56,3
Ni	µg/l	6,06
P	µg/l	<40
Pb	µg/l	0,682
Sr	µg/l	33800
V	µg/l	0,0671
Zn	µg/l	47,5
La	µg/l	0,566
Ce	µg/l	0,131
Pr	µg/l	<0.05
Nd	µg/l	<0.05
Sm	µg/l	<0.05
Eu	µg/l	<0.05
Gd	µg/l	<0.05
Tb	µg/l	<0.05
Dy	µg/l	<0.05
Ho	µg/l	<0.05
Er	µg/l	<0.05
Tm	µg/l	<0.05
Yb	µg/l	<0.05
Lu	µg/l	<0.05
Sc	µg/l	<0.5
Rb	µg/l	37,6
Y	µg/l	0,291
Zr	µg/l	3,6
Sb	µg/l	0,498
Cs	µg/l	5,94
Hf	µg/l	0,835
Tl	µg/l	<0.05
U	µg/l	0,274
Th	µg/l	<0.2
Br	µg/l	42500
I	µg/l	115
Cl	mg/l	5923
SO4	mg/l	409
SO4-S	mg/l	137

APPENDIX E: Chemical analysis of KA3065A03:2 sample 2005-09-15

ELEMENT	SAMPLE	KA3065A03:2 2005-09-15 LTDEGuard sect
Ca	mg/l	1880
Fe	mg/l	<0.004
K	mg/l	10,9
Mg	mg/l	45,4
Na	mg/l	1900
S	mg/l	132
Si	mg/l	5,6
Al	µg/l	4,13
Ba	µg/l	83,2
Cd	µg/l	0,163
Co	µg/l	0,194
Cr	µg/l	0,225
Cu	µg/l	1,69
Li	µg/l	1340
Mn	µg/l	279
Mo	µg/l	69
Ni	µg/l	25,7
P	µg/l	<40
Pb	µg/l	<0.3
Sr	µg/l	33600
V	µg/l	0,0573
Zn	µg/l	8,75
La	µg/l	0,0702
Ce	µg/l	<0.05
Pr	µg/l	<0.05
Nd	µg/l	<0.05
Sm	µg/l	<0.05
Eu	µg/l	<0.05
Gd	µg/l	<0.05
Tb	µg/l	<0.05
Dy	µg/l	<0.05
Ho	µg/l	<0.05
Er	µg/l	<0.05
Tm	µg/l	<0.05
Yb	µg/l	<0.05
Lu	µg/l	<0.05
Sc	µg/l	<0.5
Rb	µg/l	38,1
Y	µg/l	0,246
Zr	µg/l	2,41
Sb	µg/l	0,398
Cs	µg/l	3,67
Hf	µg/l	0,601
Tl	µg/l	<0.05
U	µg/l	0,278
Th	µg/l	<0.2
Br	µg/l	42700
I	µg/l	243
Cl	mg/l	6152
SO4	mg/l	943
SO4-S	mg/l	314

