

Appendix 4

Chemical Conditions in the A2 Parcel of the Long-Term Test of Buffer Material in Äspö (LOT)

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ABSTRACT

The Long-Term Test of Buffer Material (LOT) is underway in the Äspö Hard Rock Laboratory in Sweden to test the buffer material for nuclear waste disposal. The test parcels contain prefabricated bentonite blocks placed around a copper tube. A heater is placed in the lower part of the copper tube in order to simulate the heating effect of the spent fuel. The parcels are 300 mm in a diameter and placed in 4 m-long vertical boreholes in granitic rock at a depth of 450 m. This report concerns the chemical studies performed on the parcel A2, which was excavated after about five years of experiment period. Two sample blocks were taken from the hot part of the parcel for studies. One of them was without additives while in the other one, cement plugs had been placed.

In the block without additives the water content, which was close to the heater 28 – 30 wt% of the dry bentonite, increased to 32 – 33 wt% close to the rock. The total concentrations of dissolving chloride and sulphate in bentonite were determined by dispersing bentonite samples in deionized water. It was obvious that sulphate had redistributed and precipitated close to the heater during the experiment. The initial chloride concentration of bentonite had increased during the experiment approximately by a factor of ten. The increase in the chloride concentration was caused by chloride in the saturating groundwater. Porewaters were squeezed out from the bentonite samples and their Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and HCO_3^- concentrations determined. The chloride, sodium and potassium concentrations were rather independent of the distance from the heater. The calcium, magnesium and sulphate concentrations increased and bicarbonate concentrations decreased proceeding from the outer surface towards close to the heater. The chloride concentration in the squeezed porewater was slightly higher than that determined by the dispersion method, but about half of the concentration in the Äspö groundwater. The Eh and pH were measured directly in bentonite samples. Close to the outer surface, the pH in the bentonite was 7.2 and increased to 8.3 close to the heater. The Eh measurements suggest that the conditions in the bentonite were reducing. With the gold electrode, the Eh varied from -183 to -228 mV and with the Pt electrode from -287 to -366 mV, where the more negative values represent the conditions close to the heater.

In the block with the cement plugs the water content was somewhat higher than in the block without cement, which may be caused by the effect of the lower temperature in the block with cement. The concentrations of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and HCO_3^- in the squeezed porewaters were practically independent of the distance from the cement but clearly higher than in the block without cement. The pH values were generally somewhat higher than in the block without cement, and the increase was clearly seen in the measurement point closest to the cement.

Key words: nuclear waste, disposal, bentonite, buffer, porewater chemistry, rock laboratory

TIIVISTELMÄ

Äspön kalliolaboratoriossa Ruotsissa on menossa pitkäaikainen puskurimateriaalin testaus n.s. LOT-koe ydinjätteen loppusijoitusta varten. Testisyliinterit on tehty esivalmistetuista bentoniittipaloista, jotka on asetettu kupariputken ympärille. Kupariputken alaosaan on asetettu kuumemmin. Bentoniittisyliinterit ovat 300 mm halkaisjaltaan ja ne on asetettu neljä metriä pitkiin, pystysuoriin porareikiin graniittikallioon 450 metrin syvyyteen. Tässä raportissa käsitellään kemiallisia tutkimuksia, joita tehtiin sylinterille A2, joka kaivettiin ylös viisi vuotta kestäneen koejakson jälkeen. Kaksi näytepalaa otettiin tutkimuksiin bentoniittisyliinterin kuumasta osasta. Toinen niistä oli ilman lisäaineita ja toiseen oli asetettu sementtisyliinterejä.

Palassa ilman lisäaineita vesipitoisuus lämmittimen lähellä oli 28-30 paino-% bentoniitin kuivapainosta, josta se kasvoi 32-33 prosenttiin kallion läheisyydessä. Liukenevan kloridin ja sulfaatin kokonaispitoisuudet bentoniitissa määritettiin dispersoimalla bentoniittinäyte deionisoituun veteen. Sulfaattipitoisuudet olivat jakaantunut uudelleen kokeen aikana siten, että sulfaatti oli saostunut lämmittimen lähelle. Bentoniitin alkuperäinen kloridipitoisuus, oli kasvanut kokeen aikana noin kymmenenkertaiseksi. Kloridin kasvanut pitoisuus bentoniitissa aiheutui kyllästävän pohjaveden mukana tulleesta kloridista. Huokosvesiä puristettiin bentoniittinäytteistä ja niistä määritettiin Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and HCO_3^- pitoisuudet. Kloridi-, natrium- ja kaliumpitoisuudet puristetuissa huokosvesissä olivat melko riippumattomia etäisyydestä lämmittimestä. Kalsium, magnesium ja sulfaattipitoisuudet kasvoivat ja bikarbonaattipitoisuudet pienenivät siirryttäessä ulkopinnalta lämmittimen läheisyyteen. Kloridipitoisuus puristetussa huokosvedessä oli hiukan suurempi kuin dispersiomenetelmällä määritetty, mutta noin puolet Äspön pohjaveden pitoisuudesta. Eh ja pH mitattiin suoraan bentoniittinäytteistä. Ulkopinnan läheisyydessä pH oli 7.2, josta se kasvoi arvoon 8.3 siirryttäessä lämmittimen läheisyyteen. Eh-mittausten mukaan olosuhteet bentoniitissa olivat pelkistävät. Kultraelektrodilla Eh vaihteli -183 millivoltista -228 millivolttiin ja platinaelektrodilla -287 millivoltista -366 millivolttiin, missä negatiivisemmat arvot edustavat olosuhteita lämmittimen lähellä.

Palassa, johon sementtisyliinterejä oli lisätty, vesipitoisuus oli hiukan korkeampi kuin palassa ilman sementtiä, mikä saattaa johtua alhaisemmasta lämpötilasta. Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} ja HCO_3^- pitoisuudet puristetuissa huokosvesissä olivat käytännössä riippumattomia etäisyydestä sementistä. Bentoniitissa mitatut pH-arvot olivat yleensä hiukan korkeampia palassa, jossa oli sementtiä, ja kasvu oli selvästi nähtävissä mittauspisteessä, joka oli lähinnä sementtiä.

Avainsanat: ydinjäte, loppusijoitus, bentoniitti, puskuri, huokosvesikemia, kalliolaboratorio

PREFACE

The Long-Term Test of Buffer Material (LOT) is underway in the Äspö Hard Rock Laboratory in Sweden, which is organized by the Swedish Nuclear Fuel and Waste Management Co. (SKB). The project is coordinated by Clay Technology AB and many other partners are participating in the project. The Finnish nuclear waste company, Posiva Oy, is participating in the project through the work carried out by VTT.

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Tiivistelmä

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1 INTRODUCTION

The Long-Term Test of Buffer Material (LOT) project is underway in the Äspö Hard Rock Laboratory in Sweden. The LOT test series may be described as a multi-task experiment in which test parcels are exposed to conditions similar to those in a KBS3-repository and to conditions that accelerate the alteration processes, respectively. The test parcels contain prefabricated bentonite blocks placed around a copper tube, which are placed in vertical boreholes in a granitic rock structure. The diameters of the holes are 300 mm and the depths around 4 m. In total, the test series includes seven test parcels (Table 1) of which three are exposed to standard KBS-3 conditions and four test parcels are exposed to adverse conditions. The two pilot tests (A1 and S1) and the main test A0 have already been completed (Karnland et al. 2000, Muurinen 2003). All five later test parcels (A0, S2, S3, A2 and A3) have in principle identical constructions, except for a number of different additives at specific locations in the bentonite blocks in the A-type parcel (Figure 1). Small titanium ampoules equipped with titanium filters, were also placed at strategic positions in the bentonite in order to get representative water samples from the bentonite at test termination. Temperature, total pressure, water pressure, and water contents, are measured during the heating period. At test termination, the parcels are extracted by overlapping core drilling around the original borehole, and the parcels are lifted and partitioned. Material from defined positions in the test parcels and reference material are thereafter examined by a general, well-defined set of tests and analyses in order to provide data for the different objectives.

This report concerns studies performed by VTT on the A2 parcel, which was excavated between December 2005 and January 2006 after about five years' operation. The aim of the work carried out by VTT in the LOT project is to obtain data about the chemical conditions to be developed in bentonite. Porewaters were squeezed out from the bentonite samples next to the ampoules and cement additives placed in the bentonite and their chemical compositions determined. Measurements of pH and Eh were performed directly in the bentonite samples. Dissolving chloride and sulphate in bentonite were determined by the dispersion method.

Table 1. Specification of the LOT test series.

type	No	Type	T, °C	P _c	time, y	Remark
S	1	standard	90	T	1	Finalized
S	2	standard	90	T	~ 5	Ongoing
S	3	standard	90	T	~ 20	Ongoing
A	0	adverse	120<150	T, ([K ⁺], Am, pH)	1	Finalized
A	1	adverse	120<150	T, ([K ⁺], Am, pH)	1	Finalized
A	2	adverse	120<150	T, ([K ⁺], Am, pH)	~ 5	Analyzing
A	3	high T	120<150	T	~ 5	Ongoing

S = standard conditions
P_c = controlled parameter
Ma = mineralogical alteration

A = adverse conditions
C = cementation
Am = accessory minerals

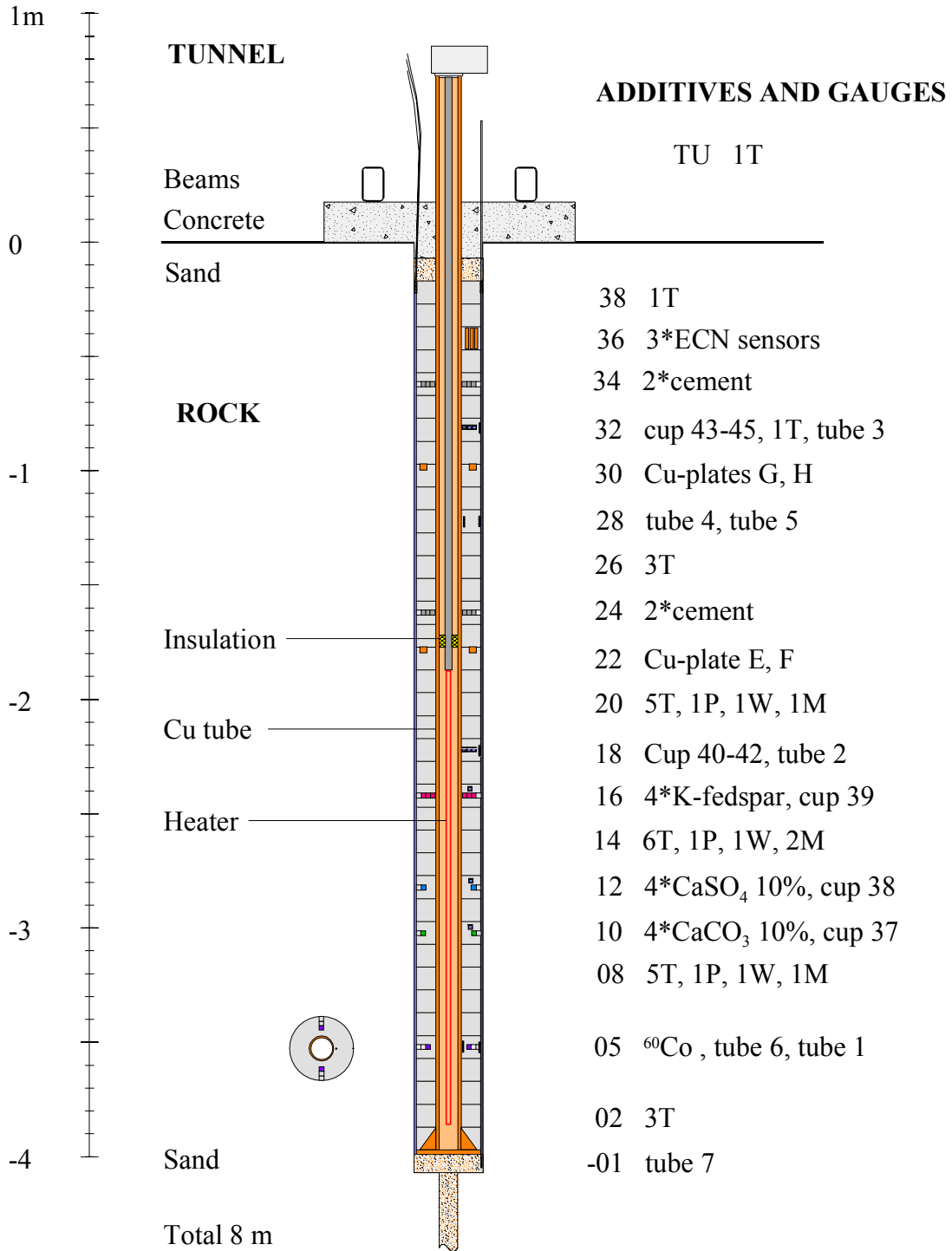


Figure 1. Principle scaled layout of the A2 test parcel. Numbers on the right-hand side of the parcel indicate the block number and the following text refers to sensors and additives.

2 EXPERIMENT WITH THE A2 PARCEL

Figure 1 presents the construction of the A2 parcel. Wyoming bentonite sold under the commercial name MX-80 was the source material for all the bentonite components in the system. The bentonite material was compacted so that the intended water-saturated density was 2000 kg/m^3 . In order to study the chemical changes caused by cement in the bentonite, cement plugs cast from Aalborg white Portland cement and deionized water in the cement-water ratio of 0.8 were placed in the bentonite. The plugs were placed in cylindrical holes, which were drilled from the mantle surface into the specified blocks.

The A2 parcel was placed in the KG0037G01 test hole situated in the G-tunnel at -450 m level in 29 Oct. 1999. The power to the heater was turned on 2 Feb 2000, and was increased in steps to 850 W. Stable temperature conditions were reached after one year, and the final temperature distribution shown in Figure 2 represents fairly well the conditions during the whole 5-year test period. The power was turned off 5 Dec 2005 in order to facilitate the uplift and sampling. Percussion drilling was started 9 Jan 2006 in order to uncover a rock column around the A2 test parcel. The column was released at the bottom by thread-sawing and finally lifted 16 Jan 2006. The rock cover was removed starting the following day 17 Jan 2006, and a rough partition of the clay was made at the test site. The remaining part was divided into sections, as similar to the original 10 cm-high blocks as possible, using saws and knives. Block 18 without additives and half of block 24 with one cement plug were carefully placed in metal vessels, flushed with N_2 and sent to VTT. The temperature of block 24 was somewhat lower than that of block 18, as seen in Figure 2, which is based on the field data of the LOT experiment.

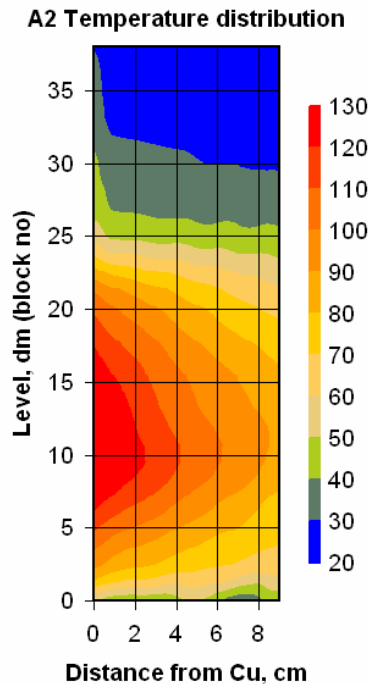


Figure 2. Temperature distributions in parcel A2 just before termination of the power.

3 STUDIES ON BENTONITE SAMPLES

3.1 Splitting of the bentonite blocks

The bentonite samples were sent by Clay Technology AB to VTT in metallic transportation vessels flushed with nitrogen for oxidation shielding. At VTT, the bentonite was moved into a nitrogen glove box (N-box, O₂ about 500 ppm) for splitting. The bentonite samples were cut in the N-box with a band saw. Sample vessels of 125 ml, which had been in nitrogen atmosphere for removal of the oxygen from their surfaces, were used for storage of the sample pieces.

Figure 3 presents the splitting of block 18. First the sectors containing the titanium cups were cut away and the cups removed. A hole was bored into the sinter of the cup, and through this hole a pipette was used to remove the water. However, it appeared that all the sinter cups were empty.

Sector SE between the sinter cups 40 and 41 was selected to be used in the studies and sector S between cups 41 and 42 for back-up samples. The upper and lower layers (A, C) were removed from sector SE. Then a thin horizontal layer (B2) was cut from sector SE. Two bars were cut from B2 and used for preparation of 1 cm-long dispersion samples and water content samples extending from the copper tube to the outer surface. The rest of the

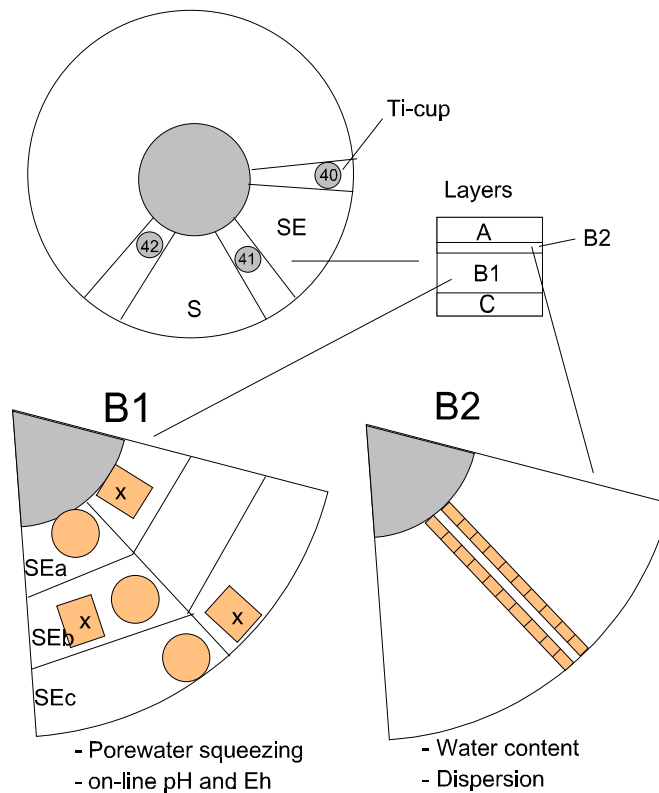


Figure 3. Splitting of block 18.

middle layer (B1) was cut into six sub-samples, which represent the radial distances 0–3.3 cm (SEa), 3.3–6.6 cm (SEb) and 6.6–10 cm (SEc) from the copper tube. The sub-samples were closed in plastic vessels, which were moved to an N₂ glove box (Braun glove -box, O₂ < 1 ppm) and opened there for a while in order to change the gas in the vessel for one of a lower O₂ concentration. The vessels were then stored in the Brown glove box until used for porewater squeezing and the samples of direct pH and Eh measurements.

Figure 4 presents splitting of the northern half of block 24, where one of the cement plugs was placed. The upper and lower layers (A, C) were first removed and the middle layer B used for the samples. The samples to be studied were cut from both sides of the cement plug. To the left of the cement, three sectors were sawn from B1 so that the thickness of the plate was 20 mm at the radial distance of 50 mm from the copper tube. The sectors were then cut into nine sub-samples (NW1 to NW9), which represent the radial distances 0–3.3, 3.3–6.6 and 6.6–10 cm from the copper tube. The samples were stored in the Brown glove box until used for porewater squeezing.

To the right of the cement three pieces of thicknesses 2.5 cm, 2 cm and 2 cm were cut from B2. The pieces were then cut into nine sub-samples (NE1 to NE9), which represent the radial distances 0–3.3, 3.3–6.6 and 6.6–10 cm from the copper tube. The samples were stored in plastic vessels in the Brown glove box until used for pH measurement. Below B2, a thin piece B3 was cut. Two bars were cut from it and used for preparation of the water content samples extending from the copper tube to the outer surface (NE1 - NE9) and from cement to the direction of NE2-NE8.

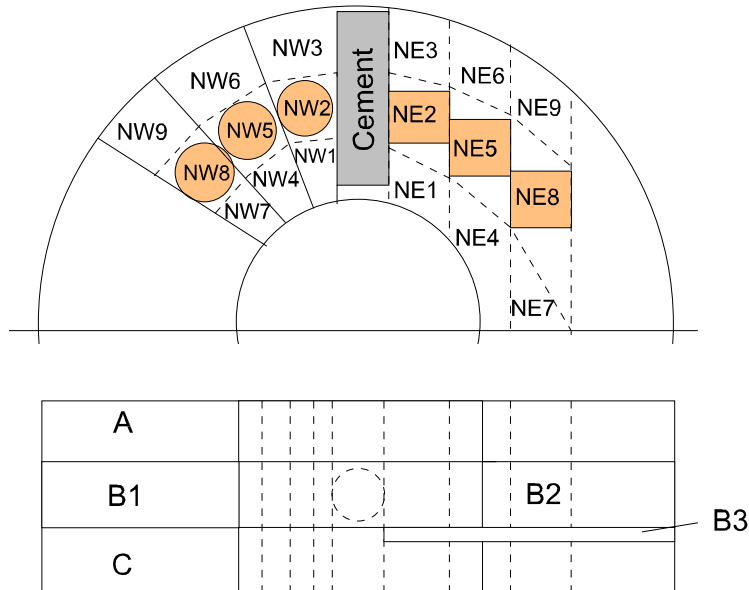


Figure 4. Splitting of block 24.

3.2 Measurement of pH and Eh in bentonite

The measurement cell used for the pH and Eh measurements in bentonite is presented in Figure 5. The cell consists of a piston, a cylindrical sample holder, a sinter and a bottom part, all made of titanium. The bottom part contains a tube, which, while filled with squeezed pore water, establishes the necessary electrical contact between the measuring electrode(s) and the reference electrode. A bentonite sample is first placed in the sample holder and compressed slightly in order to fill the sinter and the solution tube with porewater. Calibrated electrodes are then placed in the holes made in the bentonite. The bentonite is gently compacted in order to obtain a good contact between the bentonite and the electrode surface. A leak-free LF-2 reference electrode is placed in the tube and the measurement cell is placed in a metal frame, which keeps the piston in a fixed position and assures that the sample volume remains constant. Potential measurements, which normally take a couple of weeks, are carried out. Finally the electrodes are removed and recalibrated.

In block 18, three horizontal cylinders were taken at different distances from the copper tube (Fig. 3). Each of them was placed in a measurement cell. Iridium oxide pH electrodes and Eh electrodes made of gold and platinum wires were placed in the bentonite samples at distances of 1, 5 and 9 cm from the copper tube (marked with crosses in Fig. 3). In block 24, the pH values were measured at different distances from the cement plug. For this purpose, horizontal bentonite cylinders from NE2, NE5 and NE8 were put in one measurement cell and IrOx pH electrodes placed in the bentonite at distances of 0.5, 1.5, 3.5 and 5.5 cm from the cement and the radial distances of 4 – 6 cm from the copper tube.

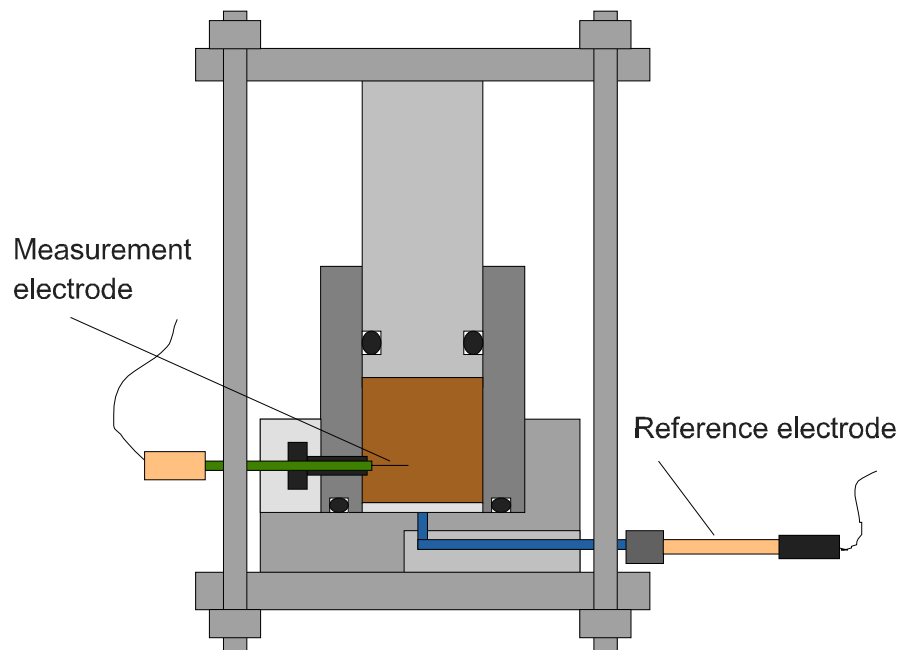


Figure 5. Schematic drawing of the measurement cell for pH and Eh measurements in bentonite.

3.3 Studies on squeezed porewaters

Squeezing of the porewaters was carried out in the nitrogen glove box (Braun box) in titanium cells, as shown in Figure 6. The pressure was increased stepwise to about 100 MPa and the porewater was collected in a syringe. From block 18, the bentonite samples from SE were taken at distances of 0–2, 4–6 and 8–10 cm from the copper tube. The squeezing samples of block 24 (NW2, NW5 and NW8) were taken at distances of 0–2, 2–4 and 4–6 cm from the cement, and 4–6 cm from the copper tube.

When squeezing was completed, the porewater sample was moved from the syringe into a centrifugal tube. The sample was centrifuged 15 000 rpm followed by ultrafiltering in a centrifuge filter tube (Whatmann, Vectra Spin™ Micro, MWCO 12 k). The ultrafiltered sample was used in the analyses. The concentrations of Na^+ , Ca^{2+} , and Mg^{2+} were determined with ICP-AES, K^+ with FAAS, Cl^- and SO_4^{2-} with IC, and HCO_3^- with titration.

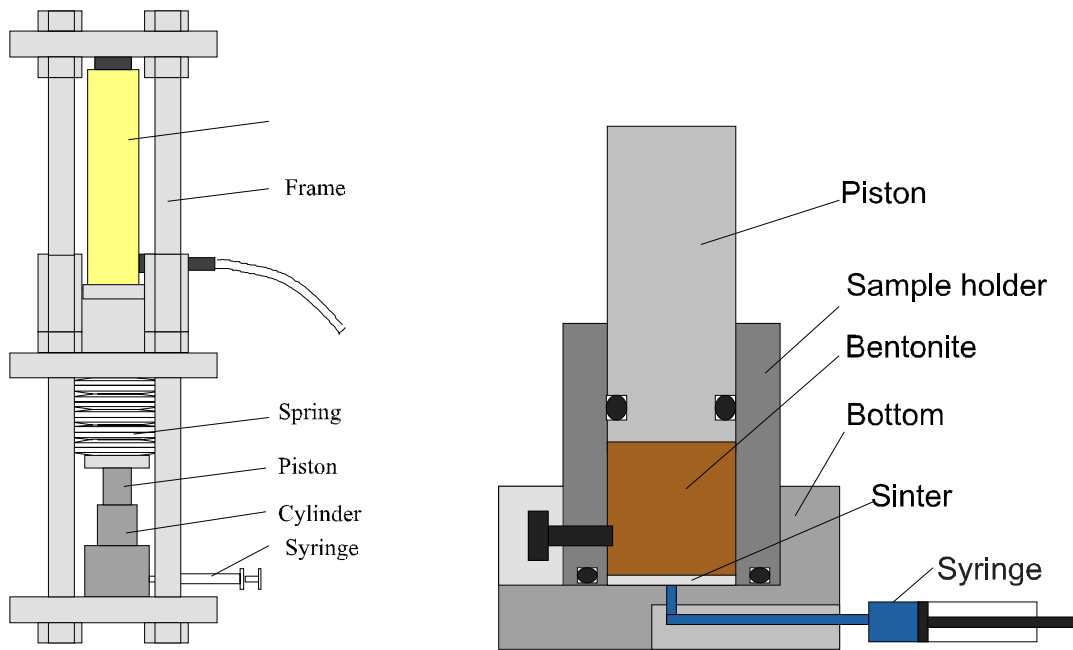


Figure 6. Schematic drawing of a pressing device and squeezing cell for porewater squeezing.

3.4 Analyses with dispersion method

The dispersion method was used for determination of the dissolving chloride and sulphate in the bentonite. The bentonite samples were taken from block 18 at different distances from the copper tube. In the measurement, about 2 g of bentonite was dispersed in 60 ml of deionized water in centrifuge tubes. The bentonite was then separated by centrifuging. The chloride and sulphate concentrations were analysed in the ultrafiltered solution samples with IC.

4 RESULTS AND DISCUSSION

4.1 Block A2 18

The results of block 18 are presented in Appendix 1. Table 1 in App.1 presents the radial distributions of water contents and chloride and sulphate concentrations determined with the dispersion method in the bentonite. The concentrations are presented both in mg per the weight of the dry clay and in mmol per the total porewater volume in the bentonite. The concentrations of different chemical components in the squeezed porewaters are presented in Table 2 of App.1, and the pH and Eh results measured directly in the bentonite samples in Table 3 of App.1. The composition of the Äspö groundwater is presented in Appendix 3.

The radial behaviour of the water contents in block 18 is clarified in Figure 7. The content is lowest about 2.5 cm from the heater tube, increasing clearly while going outwards and slightly while going closer to the heater.

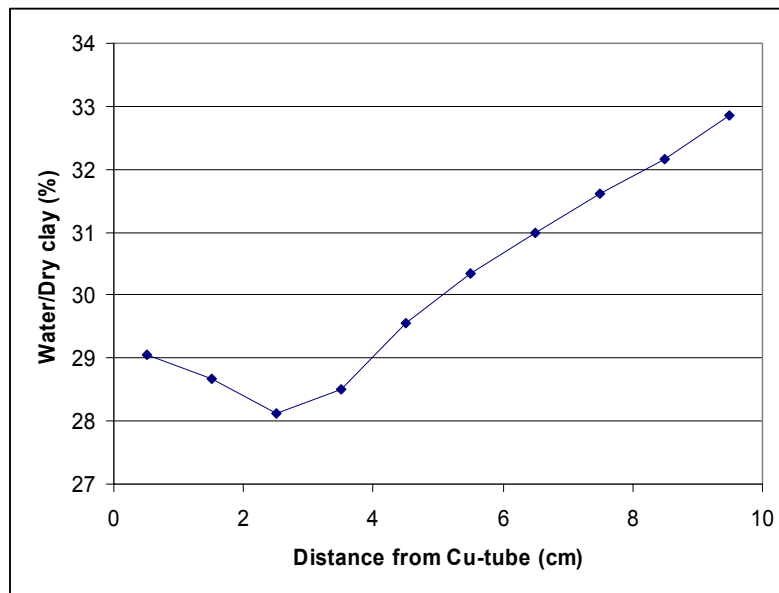


Figure 7. Radial distribution of water contents in the sample A2 18 B SE.

Figure 8 presents the SO_4^{2-} and Cl^- concentrations in the A2 18 SE sample of the LOT experiment together with the background values determined for MX-80, which had not been in the experiment. The sulphate and chloride concentrations determined with the dispersion method are presented in mg per the weight of the dry clay. In Figures 9 and 10 the SO_4^{2-} and Cl^- concentrations of the LOT samples are presented per the volume of the porewater in the bentonite and compared with the background concentrations coming from MX-80 and with the concentrations in the Äspö groundwater.

When the initial sulphate concentration in the bentonite was about $4 \text{ mg/g}_{\text{dry clay}}$, it increased during the experiment to about $12 \text{ mg/g}_{\text{dry clay}}$ close to the heater, and decreased to about $0.7 \text{ mg/g}_{\text{dry clay}}$ in the outer parts of the cylinder. The concentration in the Äspö groundwater is clearly lower than the concentrations coming from the dissolving sulphate in the bentonite, as seen in Figure 9. It is obvious that sulphate has redistributed during the experiment. This type of behaviour can be expected during non-isothermal conditions when the solubility depends on the temperature. Accumulation occurs in the area of the lower solubility. Modelling by Domènech et al. (2004) and Arthur and Zhou (2005) support this observation. The place of the concentration maximum may be affected also by other simultaneous dissolution/precipitation reactions, where the same ion participates (Arthur and Zhou, 2005).

The initial chloride concentration ($0.07 \text{ mg/g}_{\text{dry clay}}$) increased during the experiment approximately by a factor of ten (Fig.8). The concentration of Äspö groundwater is about three times that found in the LOT samples, as seen in Figure 10. It is obvious that the increased chloride in the bentonite is caused by chloride coming with the saturating groundwater. The concentration in the outer part of the bentonite is somewhat higher than that in the inner part, which may be caused by the diffusion gradient from the groundwater to the bentonite.

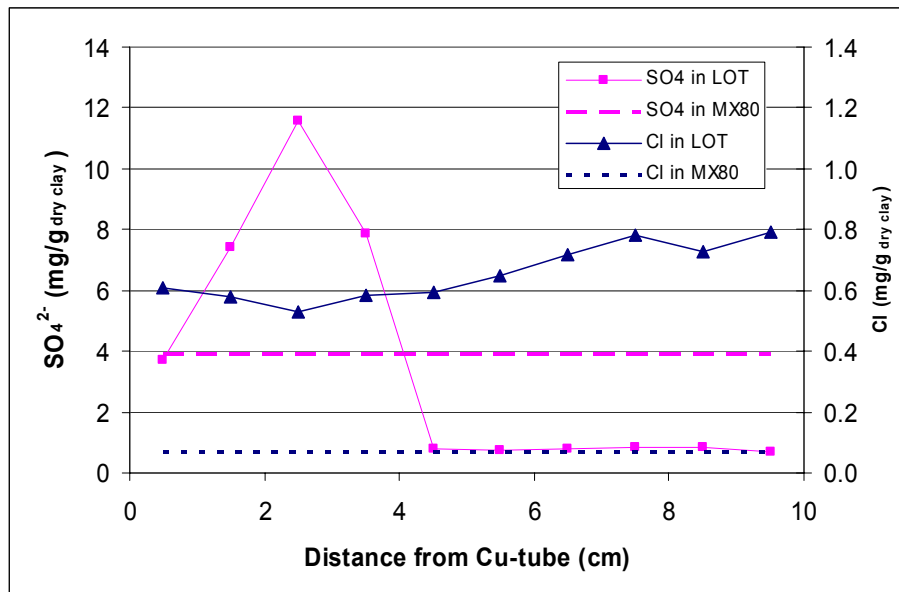


Figure 8. Sulphate and chloride concentrations in LOT sample A2 18 B SE as a function of the distance from the copper tube. The results are compared with the concentrations in MX-80 bentonite not been in the experiment. The concentrations were determined with the dispersion method and are presented per the weight of the dry clay.

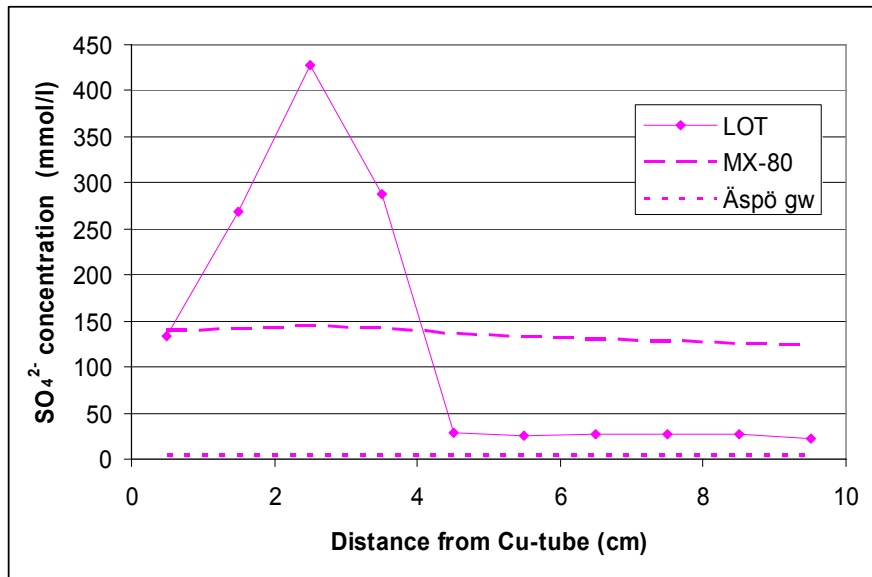


Figure 9. Sulphate concentration in sample A2 18 B SE as a function of the distance from the copper tube determined with the dispersion method and presented per the volume of the porewater (LOT) concentration, which sulphate of MX-80 would cause when evenly dissolved in the porewater (MX-80), and sulphate concentration in Äspö groundwater (Äspö gw).

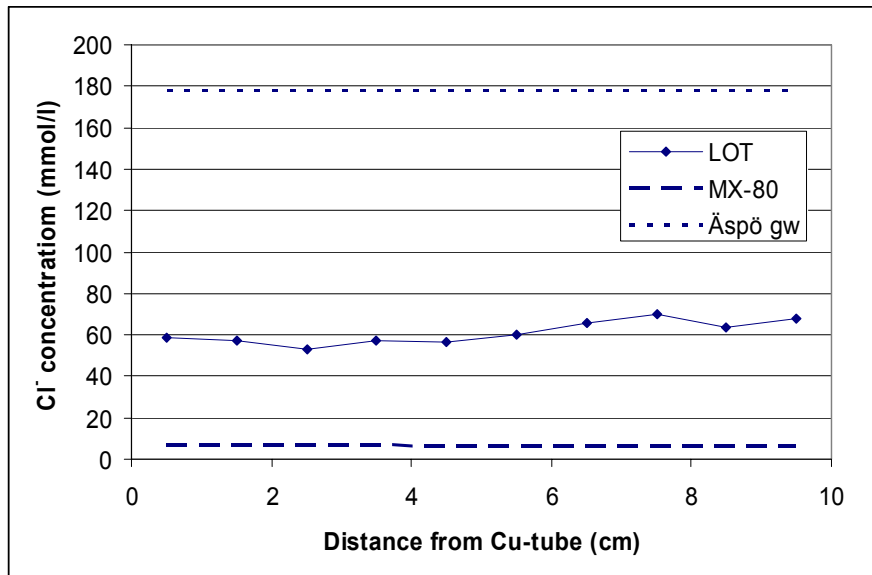


Figure 10. Chloride concentrations in sample A2 18 B SE as a function of the distance from the copper tube determined with the dispersion method and presented per the volume of the porewater (LOT) concentration, which chloride of MX-80 would cause when evenly dissolved in the porewater (MX-80), and chloride concentration in Äspö groundwater (Äspö gw).

The concentrations in the squeezed porewaters are presented in Figures 11 and 12 as a function of the distance from the copper tube. Some trends can be seen in the figures. The chloride, sodium and potassium concentrations are rather independent of the distance from the heater. The chloride concentration of the squeezed porewater is slightly higher than that determined by the dispersion method seen in Figure 10 but about half of the concentration in the Äspö groundwater. It is most probable that all the chloride is dissolved.

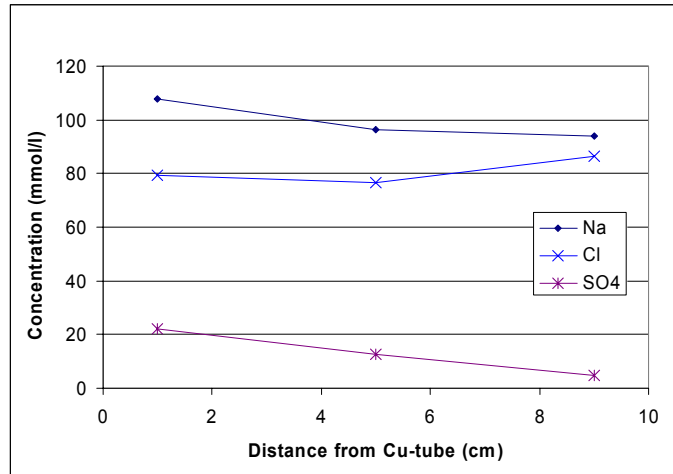


Figure 11. Radial distributions of concentrations of major components in the squeezed porewaters of samples A2 18 B SE.

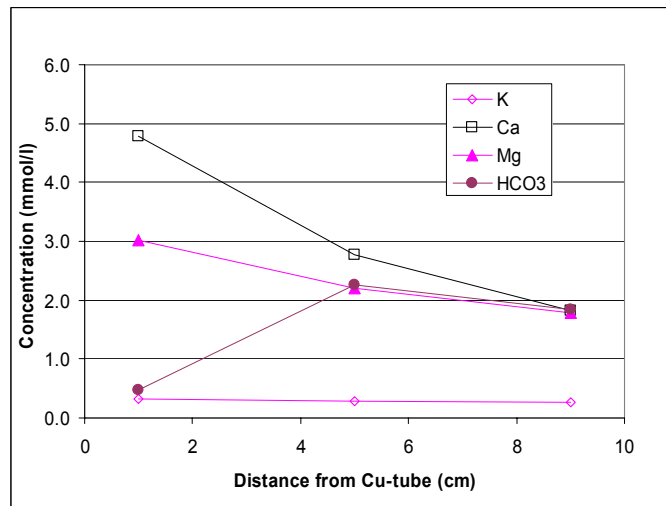


Figure 12. Radial distributions of the concentrations of the minor components in the squeezed porewaters of samples A2 18 B SE.

Calcium, magnesium and sulphate concentrations increase proceeding from the surface to the direction of the heater. The sulphate concentration in the squeezed porewater is much lower than the value in Figure 9, which assumes that all of the sulphate is dissolved. It is obvious that sulphate close to the heater is only partly dissolved and most of it is precipitated. Close to the outer surface the concentrations in the squeezed porewater approaches that in the Äspö groundwater. Bicarbonate in the squeezed porewater first increases proceeding inwards, but in the innermost sample the concentration clearly drops.

The radial distributions of pH and Eh determined directly in sample A2 18 B SE are presented in Figure 13. There seems to be variation in pH from slightly over 7 pH close to the outer surface to slightly over 8 pH close to the heater.

The Eh measurements suggest that the conditions in the bentonite were reducing. There is, however, systematic difference of about 100 mV in the Eh values determined with Pt and Au electrodes. With the gold electrode, Eh vary from -183 to -228 mV, and with the Pt electrode from -287 to -366 mV where the more negative values are close to the heater.

The complex microstructure of bentonite with different pore types (interlamellar, external), exclusion effects caused by electrical double layers and possible dissolution of solid material during squeezing make interpretation of the analysis results of the squeezed porewaters difficult. During squeezing of the LOT samples, the water content decreased from about 30 wt% to 23 wt% (water/dry bentonite), which means that about 20 % of the water has been removed and the dry density changed from 1500 kg/m³ to 1700 kg/m³. Probably that amount of porewater cannot come only from the external pores. It can be assumed that the squeezed water is a mixture of water coming from the large pores and that from the interlamellar space. This assumption is supported by XRD

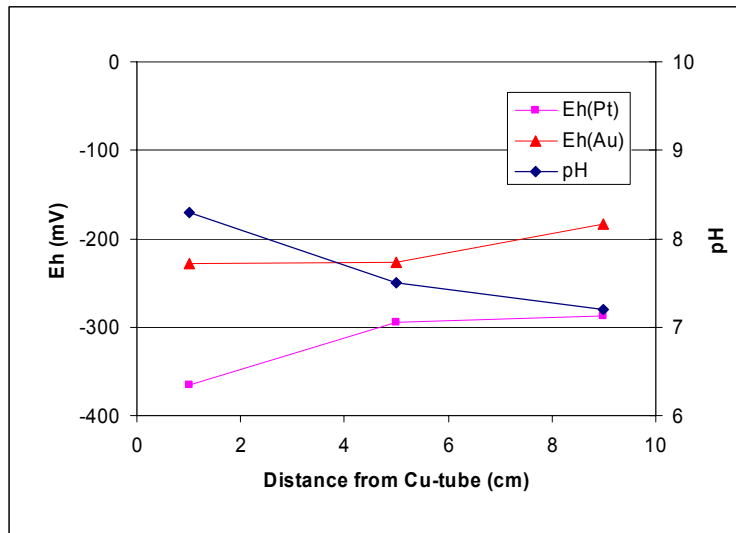


Figure 13. Radial distributions of pH and Eh determined directly in sample A2 18 B SE.

measurements performed on the bentonite samples of different densities by Kozaki et al. (1997). Muurinen et al. (2004) has evaluated that if a bentonite sample of a dry density 1500 kg/m^3 is squeezed to a density of 1900 kg/m^3 about half of the water comes from the interlamellar space. Because the concentration of free ions in the interlamellar space is very low, it dilutes the solution coming from the large pores. Owing to the electrical double layers on the montmorillonite surfaces, the free ions are not evenly distributed in the large pores either. The concentrations are higher further from the surfaces, i.e. in the middle of the pores. In squeezing, solution comes first from the middle of the pores and consequently the concentration in the solution squeezed from a large pore is higher than the average concentration in that pore. When the water coming from the external pore is diluted with that coming from the interlamellar space the concentration of some components may drop below their solubility limit. New dissolution can then occur if solid material is available. This could explain the increasing concentrations of Ca^{2+} , Mg^{2+} and SO_4^{2-} proceeding from the outer parts closer to the heater.

4.2 Block A2 24

The results of block 24 are presented in Appendix 2. Tables 1 and 2 in App.2 present the distributions of the water contents in the bentonite as a function of the distance from the heater and as a function of the distance from the cement, respectively. Table 3 in App.2 presents the measured concentrations of different chemical components in the squeezed porewaters and Table 4 shows the measured pH values in the bentonite at different distances from the cement.

The radial behaviour of the water contents in block 24 is clarified in Figure 14. The water content is about constant from 0 to 5 cm and then increases clearly proceeding outwards. The distribution differs from that in block 18 (Fig. 7) such that the water content is higher in block 24 close to the heater. The increased water content is probably caused by the lower temperature in block 24. The distribution of water contents vs. the distance from the cement in sample A2 24 B NE at the radial distance of 4 to 6 cm from the heater is presented in Figure 15. The water content is about 1% higher at a distance of 0 to 2.5 cm from the cement.

Almost all concentrations in the squeezed porewater are higher in block 24 than in block 18. Similar difference was noticed also in parcel A0 (Muurinen 2003). The concentrations of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and HCO_3^- are practically independent of the distance from the cement, as seen in Figures 16 and 17. The pH values are generally somewhat higher in block 24 than in block 18, and the increase is clearly seen at the point closest to the cement (Fig. 17).

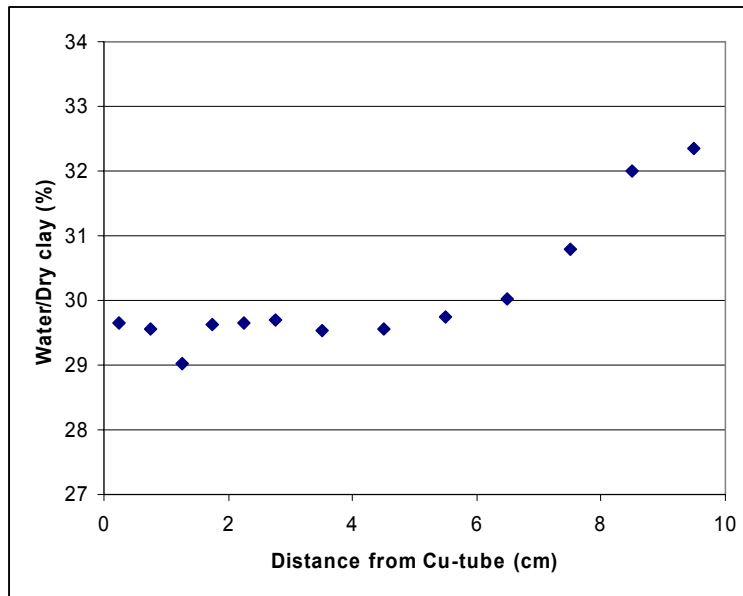


Figure 14. Radial distribution of water contents in sample A2 24 B NE.

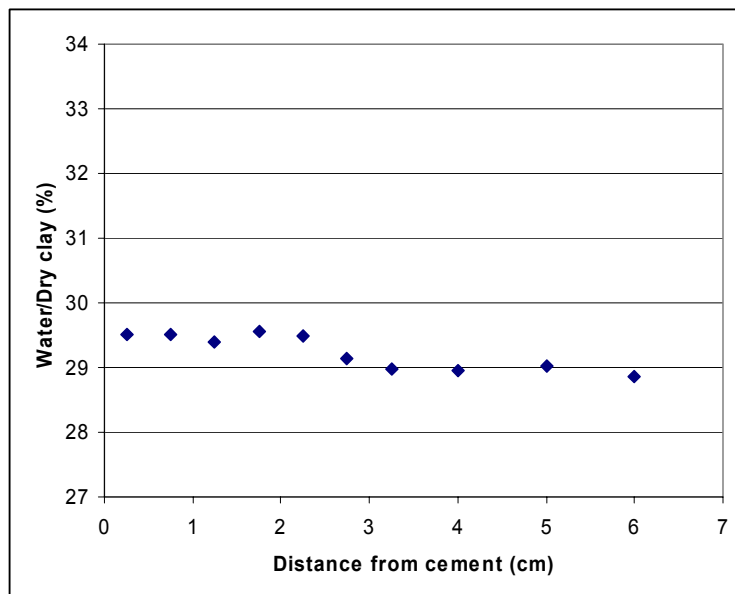


Figure 15. Distribution of water contents vs. the distance from the cement in sample A2 24 B NE at the radial distance of 4 to 6 cm from the heater.

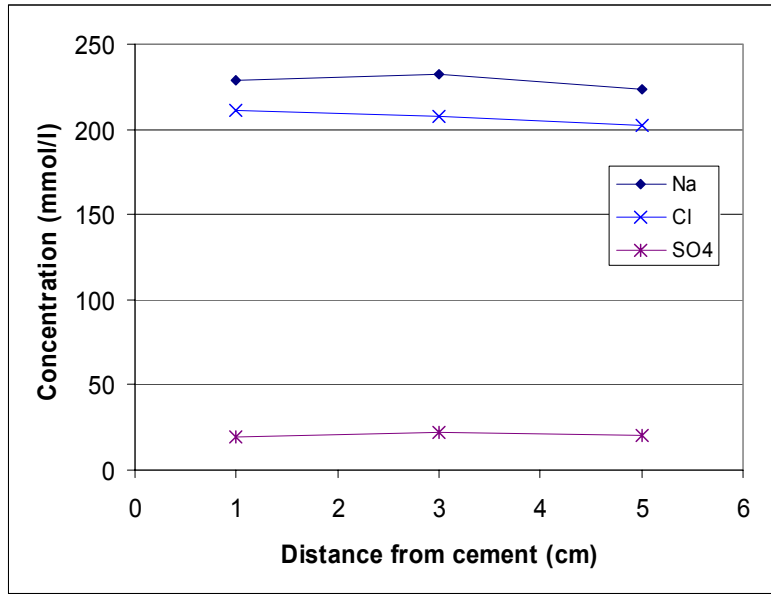


Figure 16. Concentrations of the major components in the squeezed porewaters vs. the distance from the cement plug in A2 24 B (NW2, NW5 and NW8 in Fig.4).

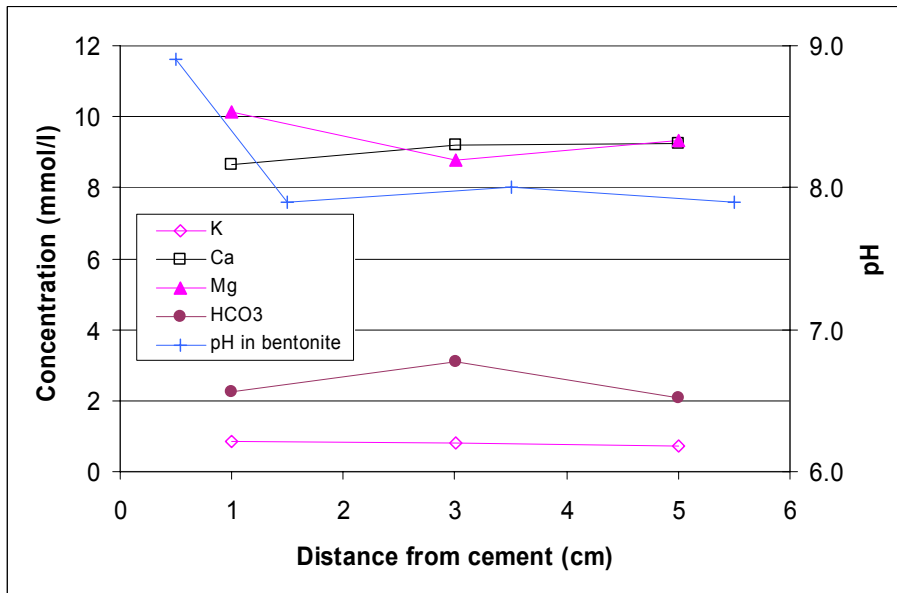


Figure 17. Concentrations of the minor components in the squeezed porewaters and pH determined directly in bentonite vs. the distance from the cement plug in A2 24 B (NW2, NW5 and NW8 in Fig. 4).

5 SUMMARY

The Long-Term Test of Buffer Material (LOT) is underway in the Äspö Hard Rock Laboratory in Sweden to test the buffer for nuclear waste disposal. The test parcels contain prefabricated bentonite blocks placed around a copper tube and a heater is placed in the lower part of the copper tube in order to simulate the heating effect of the spent fuel. The parcels are 300 mm in a diameter and placed in 4 m-long vertical boreholes in granitic rock at a depth of 450 m. This report concerns the chemical studies performed on the parcel A2, which was excavated after about five years of the experiment. Two 10 cm-high sample blocks were taken from the hot part of the parcel for studies. One of them (block 18) was without additives while in the other one (block 24), cement plugs had been placed.

In block 18 the water content which was close to the heater 28 – 30 wt% of the dry bentonite, increased to 32 – 33 wt% close to the rock. The total concentrations of dissolving chloride and sulphate contents in bentonite were determined by dispersing bentonite samples in deionized water. The initial sulphate concentration of MX-80 bentonite, 4 mg/g_{dry clay}, had increased during the experiment to about 12 mg/g_{dry clay} close to the heater, and decreased to about 0.7 mg/g_{dry clay} in the outer, colder part of the bentonite cylinder. It is obvious that sulphate had redistributed and precipitated close to the heater during the experiment. This type of behaviour can be expected during non-isothermal conditions when the solubility depends on the temperature. Accumulation occurs in the area of the lower solubility. The initial chloride concentration of bentonite, 0.07 mg/g_{dry clay}, had increased in block 18 during the experiment approximately by a factor of ten. It was obvious that the increased chloride concentration in the bentonite was caused by chloride coming with the saturating groundwater. It is most probable that all the chloride is dissolved.

Porewaters were squeezed out from the bentonite samples and their Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻ and HCO₃⁻ concentrations determined. The chloride, sodium and potassium concentrations in the squeezed porewater were rather independent of the distance from the heater. The chloride concentration was slightly higher than that determined by the dispersion method but about half of the concentration in the Äspö groundwater. The calcium, magnesium and sulphate concentrations increased and the bicarbonate concentration decreased the closer to the heater.

The Eh and pH were measured directly in bentonite samples. Close to the outer surface, the pH in the bentonite of block 18 was 7.2 increasing to 8.3 close to the heater. The Eh measurements suggest that the conditions in the bentonite were reducing. There was, however, a systematic difference of about 100 mV in the Eh values determined with Pt and Au electrodes. With the Au electrode, Eh vary from -183 to -228 mV and with the Pt electrode from -287 to -366 mV, where the more negative values represent the conditions close to the heater.

In block 24 the water content was somewhat higher close to the heater than in the block without cement. The water content was also about 1% higher close to the cement than further from it. The increased water content may be caused by the lower temperature in block 24. Almost all concentrations in the squeezed porewater were higher in block 24

than in block 18. The concentrations of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and HCO_3^- in the squeezed porewaters were practically independent of the distance from the cement. The pH values were generally somewhat higher in block 24 than in block 18, and the increase was clearly seen at the measurement point closest to the cement.

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APPENDIX 1

Results of the Block A2 18

Table 1. Radial distribution of water contents and SO_4^{2-} and Cl^- concentrations in sample A2 18 B SE. The SO_4^{2-} and Cl^- concentrations were determined with the dispersion method.

Distance from Cu-tube (cm)	Water/Clay (weight%)	Cl^- (mg/g _{dry clay})	Cl^- (mmol/l _{porewater})	SO_4^{2-} (mg/g _{dry clay})	SO_4^{2-} (mmol/l _{porewater})
0.5	29.1	0.61	58.9	3.73	134
1.5	28.7	0.58	57.2	7.40	269
2.5	28.1	0.53	53.2	11.56	428
3.5	28.5	0.58	57.6	7.87	288
4.5	29.5	0.59	56.5	0.80	28.2
5.5	30.4	0.65	60.0	0.73	25.2
6.5	31.0	0.72	65.4	0.78	26.3
7.5	31.6	0.78	69.8	0.84	27.7
8.5	32.2	0.73	63.8	0.84	27.1
9.5	32.8	0.79	67.9	0.71	22.4

Table 2. Measured concentrations of different chemical components in the squeezed porewaters of block A2 18. Point explanations: level=B, compass direction=SE, radial distances from the copper tube are 1, 5 and 9 cm.

Point	Water before squeezing (%)	Water after squeezing (%)	Na^+ (mmol/l)	K^+ (mmol/l)	Ca^{2+} (mmol/l)	Mg^{2+} (mmol/l)	Cl^- (mmol/l)	SO_4^{2-} (mmol/l)	HCO_3^- (mmol/l)
B SE 1	28.9	21.4	108	0.32	4.8	3.0	79	22.3	0.5
B SE 5	29.9	22.7	96	0.28	2.8	2.2	77	12.6	2.3
B SE 9	32.5	24.3	94	0.26	1.8	1.8	87	4.6	1.8

Table 3. Measured pH and, Eh in the bentonite of block A2 18. Point explanations: level=B, compass direction=SE, radial distances from the copper tube are 1, 5 and 9 cm.

Point	pH in bentonite	Eh_{Pi} in bentonite (mV)	Eh_{Au} in bentonite (mV)
B SE 1	8.3	-366	-228
B SE 5	7.5	-294	-227
B SE 9	7.2	-287	-183

APPENDIX 2

Results of the Block A2 24

Table 1. Radial distribution of water contents in sample A2 24 B NE.

Distance from Cu-tube (cm)	Water/Clay (weight%)
0.5	29.1
1.5	28.7
2.5	28.1
3.5	28.5
4.5	29.5
5.5	30.4
6.5	31.0
7.5	31.6
8.5	32.2
9.5	32.8

Table 2. Distribution of water contents vs. the distance from the cement in sample A2 24 B NE at the distance of about 5 cm from the copper tube.

Distance from cement (cm)	Water/Clay (weight%)
0.25	8.9
0.75	8.8
1.25	9.8
1.75	8.9
2.25	9.1
2.75	9.5
3.25	10.0
4	8.9
5	9.1
6	9.2

APPENDIX 2
continued

Table 3. Measured concentrations of different chemical components in the squeezed porewaters of block A2 24. Point explanations: level=B, compass direction=NW, radial distance=5 cm, in parentheses are the distances from the cement in cm.

Point	Water before squeezing (%)	Water after squeezing (%)	Na ⁺ (mmol/l)	K ⁺ (mmol/l)	Ca ²⁺ (mmol/l)	Mg ²⁺ (mmol/l)	Cl ⁻ (mmol/l)	SO ₄ ²⁻ (mmol/l)	HCO ₃ ⁻ (mmol/l)
B NW 5(1)	29.5	24.4	228	0.86	8.6	10.1	211	19.8	2.2
B NW 5(3)	29.1	22.8	232	0.79	9.2	8.8	208	22.3	3.1
B NW 3(5)	29.0	33.3	223	0.70	9.2	9.3	202	19.9	2.1

Table 4. Measured pH values in the bentonite of block A2 24 at different distances from the cement. Point explanations: level=B, compass direction=NE, radial distance from the copper tube =5 cm, in parentheses are the distances from the cement in cm.

Point	pH in bentonite
B NE 5(0.5)	8.9
B NE 5(1.5)	7.9
B NE 5(3.5)	8.0
B NE 5(5.5)	7.9

APPENDIX 3

Concentrations of different components in Äspö groundwater sample (Muurinen 2003). The accuracy of the analyses is $\pm 10\%$.

pH	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	SO ₄ ⁼	HCO ₃ ⁻
	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l
6.9±0.1	100	0.28	47.3	2.4	178	4.6	0.44