Development and testing of analysis methods for bentonite porewater

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Development and testing of analysis methods for bentonite porewater

Arto Muurinen
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Development and testing of analysis methods for bentonite porewater

ABSTRACT

The aim of this work was to develop and test methods for studies of the chemical properties of bentonite porewater and bentonite in The Long-Term Test of Buffer Material (LOT) project, which is underway in the Åspö Hard Rock Laboratory in Sweden.

Methods for the porewater were tested with artificial samples considering the small sample size of 1 to 2 ml, which was assumed to be available. Most of the components of interest can be determined from a squeezed porewater sample of about 1.5 ml by diluting the sample. ICP-AES appeared to be a suitable routine method for Na⁺, K⁺, Ca²⁺, Mg²⁺, Si⁴⁺ and ion chromatography (IC) for Cl⁻ and SO₄²⁻. Sulphide with spectrophotometric method likewise Fe³⁺ and Fe₅₇ with ferrozine method could be determined down to a level of 0.1 mg/l in the initial sample. Bicarbonate was determined by titration, the determination level being 1 mg/l in the initial sample.

The tests on pH showed that a sample of 0.15 ml was big enough for the microelectrode to give reliable values. The tests on Eh with reference porewaters, where different concentrations of S(-II) or Fe(II) were added, showed that the sample has to be closed carefully in the measurement cell to avoid oxidation or loss of H₂S. A sample of 0.3 ml is enough for the microelectrode. Measurement of the dissolved oxygen in diluted samples gave reliable values down to about 0.5 μg/l in the measured sample, but it is impossible to ensure that the sample stays unchanged for longer times.

A squeezing cell for porewater prepared of titanium was tested with bentonite samples and sulphide solutions. The performed tests suggest that chemical reactions between sulphide and titanium cannot be completely avoided. The reaction, however, is slow enough to allow squeezing without major changes in the sample.

Drying of bentonite by any method appeared to cause a decrease of 6-8 % in the cation-exchange capacity when determined by ion exchange with NH₄SCN dissolved in ethanol. In order to obtain comparable values, drying of all the samples at 105 °C prior to CEC determination is proposed.

A vessel was constructed and tested for transportation of the bentonite samples to be taken from the LOT experiment. The tests showed that oxidation could be avoided by closing the sample in the steel vessel in nitrogen atmosphere. To avoid movement of H₂S from the porewater to the free gas space of the vessel, the free space in the vessel as well as the storing time should be minimized.

Keywords: bentonite, porewater, analyzing, pH, Eh
Analysointimenetelmien kehitys ja testaus bentoniitin huokosvedelle

TIIVISTELMÄ

Tämän työn tarkoituksena oli kehittää ja testata menetelmiä bentoniitin huokosveden ja bentoniitin kemiallisten ominaisuuksien tutkimuksiin LOT-kokeessa (The Long Term Test of Buffer Material), joka on menossa Åspön kalliolaboratoriossa Ruotsissa.

Huokosvesille tarkoitettut menetelmät testattiin keinotekoisilla näytteillä ottaen huomioon odotetavissa oleva pieni näytekoko (1 – 2 ml). Useimmat komponentit voidaan määrittää noin 1,5 ml:n puristetusta huokosvesinäytteestä laimentamalla näyte. ICP-AES osoittautui sopivaksi rutiimen (Na+, K+, Ca2+, Mg2+, Si4+) ionien määrittelyyn. Sulfidi spektrofotometrisellä menetelmällä, samoin kuin Fe2+ ja kokonaisrauta ferrozıini menetelmällä, voidaan määrittää alkuperäisen näyteen pitoisuuteen 0,1 mg/l asti. Bikarbonaatti määritettiin titraamalla määräysrajan ollessa 1 mg/l alkuperäisessä näytteessä.

pH:ta koskevat testit osoittivat, että 0,15 ml riittää mikrolektrotille antamaan luotettavia arvoja. Eh:ta koskevat testit referenssihuokosvedellä, johon oli lisätty eri pitoisuksia S(II) ja Fe(II) ionejä, osoittivat että näyte pitää sulkea huolettisesti mittauspankkeliin hapettumisen ja H2S:n karkaamisen välttämiseksi. Riittävä näyttekkoko mikrolektrotille on 0,3 ml. Liuneenen happen mitattuna lainennenäytteestä antoi luotettava pitoisuus 1,5 μg/l pitoisuuteen asti mitattussa näytteessä, mutta on mahdotonta taata, että näyte pysyy muuttumattomana pidempia aikoja.

Huokosvesiä varten kehitetty, titaanista valmistettua puristinta testattiin bentoniittiinäytteillä ja sulfidihuokosveilla. Testit osoittivat, ettei titaania ja titaanin vältä reaktiota voida täysin välttää. Reaktio on kuitenkin tarpeeksi hidastuksen, että se sallii puristuksen ilman huomattavia muutoksia näytteessä.

Bentoniitin kuivaaminen millä tahansa menetelmällä aiheutti 6 – 8 prosentin pienenemisen kationinvaihtokapasiteetissä, kun se määritettiin suorittamalla kationinvaihto etanolilla liuotetulla NH4SCN:llä. Vertailukelpoisten arvojen saamiseksi suositellaan kaikki näytteet kuivattavaksi 105 °C:ssa.

LOT-kokeesta otettavien bentoniitinäytteiden kuljettamista varten kehitettiin ja testattiin kuljetusastia. Testit osoittivat, että hapettuminen voidaan välttää sulkeamalla näyte terävästä ympäröimän halkeiston ja H2S:n siirtyminen huokosvedestä astian vapaaseen kaasutilaan, kaasutila sekä varastointiala pitäisi minimoida.

Avainsanat: bentoniitti, huokosvesi, analysointi, pH, Eh
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FOREWORD

This study forms a part of the research programme for spent nuclear fuel disposal in Finland and Sweden. This study on bentonite porewater, funded by Posiva Oy, is the Finnish contribution to the co-operative project, Long-Term Test of Buffer Material (LOT), which is underway in the Åspö Hard Rock Laboratory in Sweden. The LOT project is organized by SKB, with Clay Technology AB acting as coordinating organization.

The author would like to thank Jukka-Pekka Salo for supervising this work. Sulo Piepponen, Heli Siren and Tarja Hiissa are also gratefully acknowledged for their contribution in the analytical work.
1 INTRODUCTION

The Long-Term Test of Buffer Material (LOT) project is underway in the Åspö Hard Rock Laboratory in Sweden (Svensk Kärnbränslehantering 1999). The testing principle is to emplace "parcels" containing a heater, central tube, precompacted clay buffer, instruments, and parameter-controlling equipment in vertical boreholes with a diameter of 300 mm and a depth of around 4 m (Figure 1). The experimental conditions are presented in Table 1. Temperature, total pressure, water pressure, and water content, are measured during the heating period. At termination of the tests, the water distribution in the clay is determined and subsequent well-defined chemical, mineralogical and physical testing are performed.

Table 1. Lay out of the planned Long-Term Test series (Svensk Kärnbränslehantering 1999).

<table>
<thead>
<tr>
<th>Type</th>
<th>No.</th>
<th>T (°C)</th>
<th>Controlled parameter</th>
<th>Time (years)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>130</td>
<td>T, [K⁺], pH, am</td>
<td>1</td>
<td>Pilot test</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>120-150</td>
<td>T, [K⁺], pH, am</td>
<td>1</td>
<td>Main test</td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>120-150</td>
<td>T, [K⁺], pH, am</td>
<td>5</td>
<td>Main test</td>
</tr>
<tr>
<td>A</td>
<td>3</td>
<td>120-150</td>
<td>T</td>
<td>5</td>
<td>Main test</td>
</tr>
<tr>
<td>S</td>
<td>1</td>
<td>90</td>
<td>T</td>
<td>1</td>
<td>Pilot test</td>
</tr>
<tr>
<td>S</td>
<td>2</td>
<td>90</td>
<td>T</td>
<td>5</td>
<td>Main test</td>
</tr>
<tr>
<td>S</td>
<td>3</td>
<td>90</td>
<td>T</td>
<td>&gt;&gt;5</td>
<td>Main test</td>
</tr>
</tbody>
</table>

A = adverse conditions  S = standard conditions
T = temperature  [K⁺] = potassium concentration
pH = high pH from cement  am = accessory minerals added

The project is coordinated by Clay Technology AB. The Finish nuclear waste company Posiva Oy will participate in the project through the work carried out by VTT Chemical technology.

The aim of the work to be carried out by VTT Chemical Technology in the LOT project is to obtain data of the chemical conditions to be developed in bentonite considering the effects of the temperature and additives. Small titanium ampoules equipped with titanium filters, were placed at strategic positions in the bentonite in order to get representative water samples from the bentonite at test termination. The waters will be moved from the ampoules in an anaerobic glove box and their compositions determined. Porewaters will be squeezed out from the bentonite samples next to the ampoules and chemical additives placed in bentonite. Their chemical compositions and occupation of the exchangeable cations of the bentonite samples will be determined. The aim of the work described in this report was to develop and test methods for studies of the water samples, porewaters and bentonites at the test termination.
**Figure 1.** Principle layout of an A-type test parcel. “T” denotes temperature gauges, “W” water pressure gauges, “P” total pressure gauges, “M” moisture gauges. The figure shows the block number (first) and number of gauges at each level (Karnland and Sandén 1997). Ampoules for water sampling have been added into the ongoing experiments (Svensk Kärnbranslehantering 1999).
2 TESTING OF ANALYTICAL METHODS FOR POREWATERS

2.1 General

The most interesting chemical parameters and components in the porewater of bentonite, are pH, Eh, O₂, Cl⁻, SO₄²⁻, S²⁻, HCO₃⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe⁺⁺, Fe⁺, Feₐₜo, Al³⁺ and Si⁴⁺. This work comprised the selection of suitable analysis methods for each chemical component and its testing considering the expected concentrations and small sample size available.

The composition of the porewater to be developed in the bentonite water interaction was evaluated by modelling. The bentonite composition used in the calculations is presented in Table 2. It is partly based on the data given by Wieland et al. (1994) and partly on the authors’ own measurements (Muurinen and Lehikoinen 1999).

Table 2. Data for MX-80 used in HYDRAQL/CE modelling, partly adopted from Muurinen and Lehikoinen 1999 (*, Wieland et al., 1994 (**), and Müller-Vonmoos and Kahr 1983 (**).  

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MX-80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation-exchange capacity, [X]ₜ</td>
<td>0.75 meq/g (*)</td>
</tr>
<tr>
<td>Amphoteric edge sites, [SOH]ₜ</td>
<td>28.4 μmol/g (**)</td>
</tr>
<tr>
<td>Edge surface area</td>
<td>3.0 m²/g (*)</td>
</tr>
<tr>
<td>Exchangeable Na</td>
<td>80.8 % (*)</td>
</tr>
<tr>
<td>Exchangeable Ca</td>
<td>12.8 % (*)</td>
</tr>
<tr>
<td>Exchangeable Mg</td>
<td>5.5 % (*)</td>
</tr>
<tr>
<td>Exchangeable K</td>
<td>0.9 % (*)</td>
</tr>
<tr>
<td>Total carbonate (as CaCO₃)</td>
<td>1.4 w% (**)</td>
</tr>
<tr>
<td>Total quartz (+ non-reactive materials)</td>
<td>23 w% (**)</td>
</tr>
<tr>
<td>CaSO₄ impurity</td>
<td>0.58 w% (*)</td>
</tr>
<tr>
<td>MgSO₄ impurity</td>
<td>0.02 w% (*)</td>
</tr>
<tr>
<td>NaCl impurity</td>
<td>0.01 w% (*)</td>
</tr>
<tr>
<td>KCl impurity</td>
<td>0.01 w% (*)</td>
</tr>
<tr>
<td>Specific density</td>
<td>2.75 Mg/m³ (**)</td>
</tr>
</tbody>
</table>

The composition of the reference groundwater in Äspö, given in Table 3, was based on Laaksoharju et al. (1998). The porewater composition was calculated by equilibrating the bentonite with the reference groundwater in a closed system. The method was based on Wieland et al. (1994). The redox reactions and exclusion effects were suppressed in the modelling. The modelling was performed using the HYDRAQL/CE computer code modified from HYDRAQL (Papelis et al., 1988) to take explicit account of cation exchange.

The reference waters were prepared from chemicals. While testing the analytical methods, the major components (Na⁺, Ca²⁺, Cl⁻, SO₄²⁻) were kept constant and the components of the lower concentration, where analytical difficulties were foreseen, were varied around the expected concentrations.
Table 3. Compositions of the reference groundwater and porewater.

<table>
<thead>
<tr>
<th>Component</th>
<th>Reference groundwater (mg/l)</th>
<th>Reference porewater (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>2100</td>
<td>6354</td>
</tr>
<tr>
<td>K</td>
<td>7.82</td>
<td>101</td>
</tr>
<tr>
<td>Ca</td>
<td>2000</td>
<td>641</td>
</tr>
<tr>
<td>Mg</td>
<td>42.1</td>
<td>147</td>
</tr>
<tr>
<td>HCO3</td>
<td>9.76</td>
<td>25.6</td>
</tr>
<tr>
<td>Cl</td>
<td>6487</td>
<td>6346</td>
</tr>
<tr>
<td>SO4</td>
<td>560</td>
<td>6897</td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Table 4 summarises the studied methods and concentrations together with the obtained determination limits and uncertainties for each component in the initial sample. While doing the tests it was assumed that the total volume of the sample is about 1.5 ml from which all the components should be determined. The detailed description of the tests for each component are given in the following chapters.

Table 4. Summary of the tests on analytical methods.

<table>
<thead>
<tr>
<th>Analysed component</th>
<th>Method</th>
<th>Water type and sample data</th>
<th>Tested conc. in the initial sample (mg/l)</th>
<th>Determination limit in the initial sample. (mg/l)</th>
<th>Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>ICP-AES</td>
<td>Ref. pw., diluted</td>
<td>6340 - 6350</td>
<td>4</td>
<td>±10 %</td>
</tr>
<tr>
<td>K⁺</td>
<td>ICP-AES</td>
<td>Ref. pw., diluted</td>
<td>0.98 - 31.7</td>
<td>14</td>
<td>±25 %</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>ICP-AES</td>
<td>Ref. pw., diluted</td>
<td>640 - 642</td>
<td>4</td>
<td>±10 %</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>ICP-AES</td>
<td>Ref. pw., diluted</td>
<td>1.5 - 121</td>
<td>4</td>
<td>±10 %</td>
</tr>
<tr>
<td>Si</td>
<td>ICP-AES</td>
<td>Ref. pw., diluted</td>
<td>Not tested</td>
<td>4</td>
<td>±10 %</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>IC</td>
<td>Ref. pw., diluted</td>
<td>5870 - 6180</td>
<td>2</td>
<td>±10 %</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>IC</td>
<td>Ref. pw., diluted</td>
<td>6890 - 6900</td>
<td>2</td>
<td>±10 %</td>
</tr>
<tr>
<td>Na⁺</td>
<td>CE</td>
<td>Ref. pw., non-diluted</td>
<td>6340 - 6350</td>
<td>30</td>
<td>±5 - 10 %</td>
</tr>
<tr>
<td>K⁺</td>
<td>CE</td>
<td>Ref. pw., non-diluted</td>
<td>0.98 - 31.7</td>
<td>50</td>
<td>±5 - 10 %</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>CE</td>
<td>Ref. pw., non-diluted</td>
<td>640 - 642</td>
<td>20</td>
<td>±5 - 10 %</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>CE</td>
<td>Ref. pw., non-diluted</td>
<td>1.5 - 121</td>
<td>1.6</td>
<td>±5 - 10 %</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>CE</td>
<td>Ref. pw., non-diluted</td>
<td>5870 - 6180</td>
<td>95</td>
<td>±5 - 10 %</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>CE</td>
<td>Ref. pw., non-diluted</td>
<td>6890 - 6900</td>
<td>100</td>
<td>±5 - 10 %</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>CE</td>
<td>Ref. pw., non-diluted</td>
<td>2.6 - 20.6</td>
<td>80</td>
<td>±5 - 10 %</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>GFAAS</td>
<td>Ref. pw., diluted</td>
<td>0.0 - 0.5</td>
<td>Not succeeded</td>
<td></td>
</tr>
<tr>
<td>Si⁴⁺</td>
<td>GFAAS</td>
<td>Ref. pw., diluted</td>
<td>0.0 - 1.0</td>
<td>Not succeeded</td>
<td></td>
</tr>
<tr>
<td>S(-II)</td>
<td>Spectroscopy</td>
<td>Ref. pw., diluted</td>
<td>0.0 - 4.6</td>
<td>0.1</td>
<td>±20 %</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>Ferrozine</td>
<td>Ref. pw., diluted</td>
<td>0.0 - 2.0</td>
<td>0.1</td>
<td>±20 %</td>
</tr>
<tr>
<td>Fe₃⁺</td>
<td>Ferrozine</td>
<td>Ref. pw., diluted</td>
<td>0.0 - 2.0</td>
<td>0.1</td>
<td>±20 %</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>Titration</td>
<td>Ref. pw., diluted</td>
<td>0.0 - 26</td>
<td>1.0</td>
<td>±20 %</td>
</tr>
<tr>
<td>pH</td>
<td>Micro electrode</td>
<td>Ref. pw., non-diluted</td>
<td>pH 7.6 - 8.4</td>
<td>Not determined</td>
<td>±0.1 pH units</td>
</tr>
<tr>
<td>Eh</td>
<td>Micro electrode</td>
<td>Ref. pw.+ S(-II), or Fe(II), non-diluted</td>
<td>S(-II) 0.14 - 5.1 Fe(II) 0.4 - 1.8</td>
<td>Not determined</td>
<td>±30 mV</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Electrode</td>
<td>Deionized water with dissolved O₂, 15 ml</td>
<td>0.0000 - 0.009</td>
<td>0.0005 (samples are not stabile)</td>
<td></td>
</tr>
</tbody>
</table>
2.2 ICP-AES and Ion Chromatography (IC)

Inductively Coupled Mass Atomic Emission Spectroscopy (ICP-AES) was used to analyze the cations and silica. In the tests, the concentrations of potassium and magnesium were varied, while the concentrations of the major components (Na⁺, Ca²⁺) were kept about constant. The sample size needed by ICP-AES is about 10 ml. In order to simulate the real situation of porewater analysis, the reference porewater sample of 0.5 ml was first diluted to 10 ml, which was given to the analytical laboratory. Further dilutions, if needed, were carried out in the analytical laboratory. Appendix A gives the results of the test.

The added and measured concentrations are compared with each other in Figure 2. The uncertainties of the concentrations of Na⁺, Ca²⁺ and Mg²⁺ were evaluated to be within ±10 % and for K⁺ ±25 %. The determination limit in the measured (diluted) sample for sodium, calcium and magnesium was 0.2 mg/l and for potassium 0.7 mg/l. Because the initial sample typically has to be diluted by a factor of 20, the determination limits in the initial porewater sample are 4 mg/l and 14 mg/l, respectively. The method can also be used for silica, where the determination limit in the measured sample is 0.2 mg/l, which means 4 mg/l in the non-diluted sample.

Ion chromatography (IC) was used to analyze chloride and sulphate. The same diluted sample, which was used in the ICP-AES, was used in the chloride and sulphate tests. The expected concentrations of those components in the porewater samples are high and the uncertainty of the result was thus the main research topic, the determination level being less interesting.

The results of the tests are presented in Appendix A and Figure 2. The uncertainties of the concentrations of chloride and sulphate were evaluated to be within ±10 %. The determination limit in the measured (diluted) sample for chloride and sulphate was evaluated to be 0.1 mg/l. Because the initial sample was diluted by a factor of 20, the determination limits in the initial porewater sample are 2 mg/l.
**Figure 2.** Testing of ICP-AES and IC for simulated porewater samples. The measured concentrations in the initial sample are compared with the added ones. The macro components are seen in the upper and minor components in the lower figure. The porewater sample of 0.5 ml was diluted to 10 ml before analyzing.
2.3 Capillary electrophoresis

Capillary electrophoresis was tested for sodium, potassium, calcium, magnesium chloride, sulphate, and bicarbonate analyses. Because only a small sample is needed in the electrophoresis the water sample used was not diluted before analyzing. The samples were the same as used in the ICP-AES and IC tests. The results are presented in Appendix B and clarified in Figure 3. The uncertainties of the concentrations in electrophoresis were evaluated to be within ±10%. The levels of reliable determination were 80 mg/l, 50 mg/l and 1.6 mg/l for HCO₃⁻, K⁺ and Mg²⁺, respectively.

Figure 3. Testing of capillary electrophoresis for simulated porewater samples. The measured concentrations in the initial sample are compared with the added ones.
2.4 Testing of GFAAS for aluminium and silica

In the test for the aluminium analysis, different amounts of AlCl3 solution containing 270 mg Al per litre were added to the reference porewater samples. These samples were then diluted so that the final concentrations of the samples varied from 0.012 to 0.1 mg/l. The samples were analyzed with an atomic adsorption spectrophotometer with graphite oven techniques (GFAAS). There was a broad scattering in the results and the method was not reliable in these conditions. The high concentrations of the macro components, precipitation and contamination are possible explanations for the bad result.

In the test for the silica analysis, different amounts of Na2SiO3 solution containing 258 mg Si per litre were added to the reference porewater samples. These samples were then diluted so that the final concentrations of the samples varied from 0.012 to 0.2 mg/l. GFAAS did not give any reasonable results. The samples were also analyzed with ICP-AES, where the highest concentration (0.2 mg/l) could be determined. The lower concentrations were below the determination level.

2.5 Sulphide analysis by a spectrophotometric method

The analysis of sulphide was tested with a method based on a standard spectrophotometric method (SFS 3038). The basis of the method is that sulphide ion forms methylene blue compound with N,N-dimethyl-p-phenylenediamine. In the test, different concentrations of S(-II) were added to the reference porewater and analyzed. In the method used, the sample of 0.25 ml was diluted in the glove-box with oxygen-free water to 3 ml, which was the minimum size required by the spectrophotometer. Figure 4 compares the measured and added S(-II) concentrations with each other.

![Figure 4. Comparison of the measured and the added S(-II) concentrations in the initial sample. An initial sample of 0.25 ml was diluted to 3 ml with oxygen-free water while preparing a sample to be measured with the spectrophotometer.](image)
The measured values were slightly higher than the theoretical ones and the uncertainty of the result is within ±20%. The determination level of the method is 0.01 mg/l in the diluted sample, which means about 0.1-0.2 mg/l in the initial sample when the sample has to be diluted due to the small size by a factor of 10 to 20.

2.6 Fe(II) and Fe_{tot} analyses by the ferrozine method

The analysis of Fe(II) and total iron (Fe_{tot}) were tested with the ferrozine method (Dimmock et al. 1979). The method is similar for both components, but in the case of Fe_{tot} the sample is treated with thioglycolic acid in order to reduce the oxidized iron. The samples were prepared by adding different concentrations of Fe(II) to the reference porewater. Both analyses were carried out from the same solutions. Prior to the analysis, the sample of 0.3 ml was first diluted in the glove-box with oxygen-free water to 3 ml, which was the minimum size required by the spectrophotometer. Figure 5 compares the measured and added concentrations with each other.

The measured Fe_{tot} corresponds well the added concentration, while Fe^{2+} concentrations are somewhat lower indicating a slight oxidation of the iron in the sample. The determination level of the method is 0.01 mg/l in the diluted sample, which means about 0.1-0.2 mg/l in the initial sample when the sample has to be diluted due to the small size by a factor of 10 to 20. The uncertainty of the results is within ±20%.

![Figure 5. Comparison of the measured and the added iron concentrations in the reference porewater. An initial sample of 0.3 ml was diluted to 3 ml with de-ionized water while preparing a sample to be measured in the spectrophotometer.](image-url)
2.7 Titration of bicarbonate

The samples used in the titration of bicarbonate were prepared by adding different concentrations of NaHCO₃ to the reference porewater. The samples were titrated with 0.0001 M HCl in an anaerobic glove-box. The equivalence point was determined with the Gran method (Appello & Postma, 1993), where the Gran function (F) is plotted against the volume of HCl added.

\[ F = (V + V_0) \times 10^{\text{pH}} \]  

where \( V \) is the volume of acid added, and \( V_0 \) is the start volume of the sample. Examples of Gran functions vs. added HCl volume for different HCO₃⁻ initial concentrations in the sample are presented in Figure 6.

Figure 7 compares the measured and added initial concentrations in the sample. In these measurements, a sample of 0.3 ml was diluted to 5 ml with de-ionized water before titration. The background of the dilution water has been subtracted from the values given in the figure.

The determination level of the method is about 1 mg/l in the initial sample when the sample is diluted by a factor of 20 before titration. The uncertainty of the result is within ±20 %.

![Figure 6. Gran functions vs. added HCl volume for different HCO₃⁻ concentrations in the sample. The initial HCO₃⁻ concentrations (mg/l) are given in the legend. A sample of 0.3 ml was diluted to 5 ml with de-ionized water before titration.](image-url)
Figure 7. Comparison of the measured and added $\text{HCO}_3^-$ concentrations in the simulated porewater. An initial sample of 0.3 ml was diluted to 5 ml with de-ionized water before titration. The background of the dilution water has been subtracted.

2.8 Measurement of pH

In the study on pH measurement, the values obtained with a microelectrode were compared with those obtained with a normal-size laboratory electrode. The microelectrode was a combination electrode by Orion (Model 98-03). The length of the electrode was 83 mm and the diameter of the tip 2.5 mm. Two sample volumes, 10 ml and 0.15 ml, were used in the measurements with the microelectrode. The normal-size electrode was an Orion Ross combination electrode. The sample size used in the measurements with the normal-size electrode was 10 ml. Both electrodes were calibrated with commercial pH buffers (pH 10 and 7) before measurement. The solutions used in the measurements were reference porewaters to which $\text{HCO}_3^-$, $\text{Na}_2\text{S}$ and $\text{FeCl}_2$ were added. This also caused the pH to vary somewhat. During the measurements, the samples were mixed with a magnetic stirrer. The measurement time required was typically a few minutes.

Figure 8 compares the pH values measured using a normal-size electrode with those measured using a microelectrode in different sample volumes. The values match each other rather well. A sample of 0.15 ml was big enough for the microelectrode to give reliable values. The uncertainty of the result is within $\pm 0.1$ pH units.
Figure 8. Comparison of pH values measured using a normal-size electrode in a sample of 10 ml with those measured using a microelectrode in samples of 10 ml and 0.15 ml.

2.9 Measurement of Eh

In the study on Eh measurement the values obtained with a microelectrode in a small and large sample were compared with those obtained with a normal-size laboratory electrode in a large sample. The solutions used in the measurements were reference porewaters to which different concentrations of \( S^{2-} \) or \( \text{Fe}^{2+} \) were added in order to adjust the Eh.

The microelectrode was a combination Pt-electrode by Microelectrodes Inc. (Model MI-800-710). The length of the electrode was 83 mm and the diameter of the tip 2.5 mm. Two sample volumes, 75 ml and 0.30 ml, were used in the measurements. The disappearance of \( S^{2-} \) or \( \text{Fe}^{2+} \) was a problem while using the sample of 0.3 ml even in the anaerobic glove box. To avoid this, the measurement ampoule had to be sealed tightly during measurement. Another problem was evaporation of the filling solution of the electrode and clogging of the filling hole during the long measurement in the dry anaerobic glove box. In order to avoid evaporation of the filling solution, the upper end of the electrode was surrounded with a cell containing some wet paper, which created a water-saturated space around the hole, thus reducing evaporation. Figure 9 shows the arrangements used in the measurements with the microelectrode.
Yokokawa Model SM29-Pt9 and SR20-AP24 as the reference were used as the normal-size electrodes. The sample size in those measurements was 75 ml. The sample bottle was sealed in this case too, although the measurement system was not so sensitive to the loss of S$_2^-$ or Fe$^{2+}$ as the small sample. During measurement, both the small and the large sample were mixed with a magnetic stirrer.

Figure 10 shows a typical Eh vs. measurement time curve for the microelectrode in a sulphide-containing sample of 0.3 ml together with the sulphide concentration in the sample at the beginning and at the end of the measurement. A slight loss of sulphide can be seen during measurement despite the tight sealing. The lower the initial sulphide concentration was the bigger was the relative change. A comparison of the S(-II) and $S_{tot}$ analyses suggested that the sulphur is lost in the form of H$_2$S. In principle, this can occur through any leakages into the glove-box atmosphere or by sorption into the sealing material. In our case, sorption into the sealing was the probable reason. Stabilization of the Eh electrode typically took 2 to 3 hours. After that, the effect of the loss of S(-II) on the Eh can be seen, although it is not very strong.

Figure 11 presents the dependence of Eh on the S(-II) concentration in the sample when the Eh values were measured with the micro Pt-electrode using samples of 0.3 and 75 ml and with the normal-size Pt-electrode using samples of 75 ml. The values measured with the microelectrode in small and large samples match each other well, and the microelectrode gives comparable values with the normal-size electrode, too. The amount of sulphur lost during the measurement is so small that normally it does not essentially disturb the Eh result. Correction back to the initial concentration can be done by calculation.

*Figure 9. Eh measurement with the micro Pt-electrode in the sample of 0.3 ml.*
Figure 10. Measured Eh and S(II) concentration as a function of time. The sample size was 0.3 ml.

Figure 11. Dependence of Eh on the S(II) concentration in the sample. The Eh values were measured with the micro Pt-electrode using samples of 0.3 and 75 ml and with the normal size Pt-electrode using samples of 75 ml.
Figure 12 shows a typical Eh vs. measurement time curve for the microelectrode in a sample of 0.3 ml where Fe$^{2+}$ was added. The figure also presents the concentrations of Fe(II) and Fe$_{tot}$ in the sample at the beginning and at the end of the measurement. A slight loss of both components can be seen during measurement, despite the tight sealing. Sorption/precipitation are the most probable reasons for the loss of iron.

Figure 13 presents the dependence of Eh on the Fe(II) concentration in the sample when the Eh values were measured with the micro Pt-electrode using a sample size of 0.3 ml. The Eh values clearly depend on the Fe(II) concentration of the sample in this case, too.

The uncertainty of the Eh measurements with the microelectrode in the sample of 0.3 ml was evaluated to be within ± 30 mV. The amount of iron lost during the measurement is so small that it does not essentially disturb the Eh measurement. Correction to the initial concentration can be done by calculation, too.

![Graph showing Eh vs. time and Fe(II) and Fe$_{tot}$ concentrations over time.](image)

**Figure 12.** Measured Eh, Fe(II) and Fe$_{tot}$ concentration as a function of time. The sample size was 0.3 ml.
Figure 13. Dependence of Eh on the Fe(II) concentration in the sample. The Eh values were measured with the micro Pt-electrode using samples of 0.3 ml.

2.10 Measurement of dissolved oxygen

The measurement of dissolved oxygen in small porewater samples was tested with an analyzer of Orbisphere Laboratories (Model 2606). The required volume of the sample was rather large, which means that the small porewater samples had to be diluted. Another problem was that oxygen tended to move through the liquid-gas interface.

In the test, samples of de-ionized water saturated in the air were moved into the anaerobic glove-box in closed experimental tubes. In order to obtain the desired oxygen concentration, a small sample was moved by pipette from the water tube below the water surface of a bottle filled with oxygen-free water. The dilution was mixed with a magnetic stirrer, and not shaken, in order to avoid loss of oxygen. Only one diluted sample per tube was prepared in order to avoid errors caused by the loss of oxygen after opening the sample tube. A volume of 15 ml was carefully moved from the diluted sample to the measurement bottle. The sample was mixed with a magnetic stirrer during measurement.

Figure 14 compares the measured concentrations of dissolved oxygen with the added ones in the diluted sample. The method gives reliable values down to about 0.5 µg/l in the diluted sample, which means that the detection level in the initial sample is 15 µg/l if the sample has to be diluted by a factor of 30. However, it is very difficult to ensure that the sample remains unchanged for longer times. In the case of bentonite porewater, where squeezing may take about one week, the dissolved oxygen would most probably escape from the water to any small gas space of the syringe, where the water sample is collected.
Figure 14. Comparison of measured concentrations of dissolved oxygen with the added concentration (ppb ≈ μg/l).
3 DETERMINATION OF EXCHANGEABLE CATIONS IN BENTONITE

The exchangeable cations had been determined earlier by changing the cations from bentonite with 0.2 M NH₄SCN in ethanol (Müller-Vonmoos & Kahr 1983). Ethanol instead of water was used to avoid dissolution of the accessory minerals. A loss of the cation-exchange capacity (CEC) has been noticed in some cases in our earlier studies and its reasons are unknown. Testing work was carried out to find the reason for the CEC loss and to confirm the reliability of the method.

In the test, the bentonite samples were treated with different methods before determination of the exchangeable cations. These methods comprised different combinations of drying, compaction, water saturation and grinding of compacted samples.

The exchangeable cations were determined by shaking 0.7 g of bentonite overnight with 7 ml of 0.2 mol/l NH₄SCN in ethanol in centrifuge tubes. The solution was separated from the bentonite by centrifuging and filtered. The treatment was repeated four times. Representative fractions of the separated solutions were combined and evaporated to dryness. The dry solids were dissolved in 10 ml of water and the cations analyzed with ICP-AES.

Table 5 presents the measured cation concentrations in bentonite after different pre-treatments together with the water content in bentonite while starting the cation exchange. It is obvious that drying the bentonite by any method causes a decrease of 6-8 % in total cation-exchange capacity. The values obtained by different methods after drying are comparable with each other, however. A short-term saturation in the air or 100 % RH does not seem to return the lost capacity. Compaction does not seem to have any effect on the cation-exchange capacity. The exact mechanism of the loss of the CEC is not yet known. However, in order to obtain comparable values it seems reasonable that all the samples are dried before measurement. Drying at 105 °C is proposed for a routine method.

Table 5. Concentrations of the exchangeable cations in bentonite after different pre-treatments.

<table>
<thead>
<tr>
<th>Water wt-%</th>
<th>Ca (mcq/g)</th>
<th>K (mcq/g)</th>
<th>Mg (mcq/g)</th>
<th>Na (mcq/g)</th>
<th>Total (mcq/g)</th>
<th>Pre-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.11</td>
<td>0.01</td>
<td>0.04</td>
<td>0.65</td>
<td>0.81</td>
<td>Air-dry MX-80</td>
</tr>
<tr>
<td>&lt;1</td>
<td>0.10</td>
<td>0.01</td>
<td>0.03</td>
<td>0.62</td>
<td>0.75</td>
<td>Air-dry MX-80, drying at 105 °C</td>
</tr>
<tr>
<td>&lt;1</td>
<td>0.10</td>
<td>0.01</td>
<td>0.04</td>
<td>0.62</td>
<td>0.76</td>
<td>Air-dry MX-80, drying at 60 °C</td>
</tr>
<tr>
<td>&lt;1</td>
<td>0.12</td>
<td>0.01</td>
<td>0.04</td>
<td>0.60</td>
<td>0.77</td>
<td>Air-dry MX-80, vacuum freeze drying</td>
</tr>
<tr>
<td>7</td>
<td>0.11</td>
<td>0.01</td>
<td>0.04</td>
<td>0.64</td>
<td>0.80</td>
<td>Air-dry MX-80, compaction, grinding</td>
</tr>
<tr>
<td>&lt;1</td>
<td>0.10</td>
<td>0.01</td>
<td>0.03</td>
<td>0.61</td>
<td>0.75</td>
<td>Air-dry MX-80, compaction, drying at 105 °C, grinding</td>
</tr>
<tr>
<td>&lt;1</td>
<td>0.13</td>
<td>0.01</td>
<td>0.04</td>
<td>0.59</td>
<td>0.76</td>
<td>Air-dry MX-80, compaction, water saturation, drying at 105 °C, grinding</td>
</tr>
<tr>
<td>3</td>
<td>0.13</td>
<td>0.01</td>
<td>0.04</td>
<td>0.58</td>
<td>0.76</td>
<td>Air-dry MX-80, compaction, water saturation, drying at 105 °C, saturation in the air, grinding</td>
</tr>
<tr>
<td>14</td>
<td>0.11</td>
<td>0.01</td>
<td>0.05</td>
<td>0.59</td>
<td>0.76</td>
<td>Air-dry MX-80, compaction, water saturation, drying at 105 °C, saturation in 100 % RH, grinding</td>
</tr>
</tbody>
</table>
4 STUDIES ON BENTONITE POREWATERS

4.1 Stainless steel squeezing cell

The bentonite samples were compacted to a dry density of 1.5 g/cm\(^3\) and saturated with Åspö reference groundwater. One of the samples (LB2) was prepared from MX-80 bentonite and the other one (LB4) from MX-80 to which 0.3 \% of pyrite was mixed. The experimental system used in saturation is seen in Figure 15. The bentonite sample was 20 mm in diameter and 20 mm in height. The bentonite-to-water ratio used in the saturation was 1.5 g bentonite per 1 ml of water, which means that about half of water was external water and the rest porewater.

After interaction of about 7 months, the sample was opened and the porewaters were squeezed out from the bentonite with the squeezing apparatus seen in Figure 16. The size of the equipment is such that it can be used in a normal anaerobic glove box. A strong spring is used to maintain the pressure during squeezing. The length of the frame, where the squeezing cell is fixed, is adjusted with a hydraulic pump in order to increase the pressure. The pressure is increased stepwise to about 100 MPa and squeezing takes usually one week. Figure 17 presents the pressure and the volume of the squeezed porewater as a function of time for the LB4 sample.

![Figure 15. Schematic diagram of the apparatus for water-bentonite interaction.](image)
Figure 16. Pressing apparatus (left) and compaction cell prepared from stainless steel (right) for squeezing the porewater.

Figure 17. Pressure and porewater volume as a function of time during porewater squeezing of LB4.
The analytical methods were selected on the bases of the tests described in the previous sections. Table 6 presents the methods and sample volumes used in each determination together with the obtained results. The volume of the sample used in each analysis varies somewhat due to slightly different initial sample volumes of LB2 and LB4.

When squeezing was finished, the porewater was first removed from the syringe into a centrifuge tube and the sample was centrifuged for 5 minutes.

A sample of 0.3 ml was then taken into a measurement ampoule for pH measurement, which took a few minutes. The pH electrode was then replaced by an Eh electrode and the ampoule was closed tightly. The Eh measurement was carried out in about 24 hours. Half of the solution in the Eh ampoule was then used for S(-II) measurement and the other half for Fe(II) measurement. Fe_{tot} was not determined due to the small volume of sample available.

The rest of the sample in the centrifuge tube was then ultrafiltered in a centrifuge filter tube (Whatman® 12 k MWCO). Part of the sample (0.22 – 0.36 ml) was diluted for ICP-AES and IC analyses. The rest of the sample (0.05 – 0.1 ml) was diluted to 5 ml and used for carbonate titration.

The measurement of pH was carried out without any problems. Pyrite added into the LB4 sample had no effect on Eh and the measured Eh values were about equal in both porewater samples. The S(-II) concentration was below the determination level. The Fe(II) could be determined and it corresponds rather well the measured Eh (Fig. 13). It was concluded, that oxidation or other reactions may have consumed S(-II) either during the interaction experiment or the porewater squeezing, and better systems are needed.

The major cations and anions could be determined without any problems. The concentration of potassium was below the determination level and that of Si was about at the determination level.

The total sample size of about 1 ml was somewhat too small. If possible, the bentonite sample should be selected so that the volume of the squeezed porewater sample is at least 1.5 ml. A procedure for porewater analysis is presented in Appendix C.
Table 6. Compositions of the bentonite porewaters

<table>
<thead>
<tr>
<th>Component</th>
<th>Method</th>
<th>Used vol. of LB2 (ml)</th>
<th>Measured in LB2</th>
<th>Used vol. of LB4 (ml)</th>
<th>Measured in LB4</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Micro-size glass electrode</td>
<td>0.3</td>
<td>8.3</td>
<td>0.3</td>
<td>8.3</td>
</tr>
<tr>
<td>Eh (mV)</td>
<td>Micro-size Pt electrode</td>
<td>&quot;</td>
<td>31</td>
<td>&quot;</td>
<td>46</td>
</tr>
<tr>
<td>Na⁺ (mg/l)</td>
<td>ICP-AES</td>
<td>0.22</td>
<td>2800</td>
<td>0.36</td>
<td>3400</td>
</tr>
<tr>
<td>K⁺ (mg/l)</td>
<td>ICP-AES</td>
<td>&quot;</td>
<td>&lt;15</td>
<td>&quot;</td>
<td>&lt;25</td>
</tr>
<tr>
<td>Ca²⁺ (mg/l)</td>
<td>ICP-AES</td>
<td>&quot;</td>
<td>120</td>
<td>&quot;</td>
<td>170</td>
</tr>
<tr>
<td>Mg²⁺ (mg/l)</td>
<td>ICP-AES</td>
<td>&quot;</td>
<td>40</td>
<td>&quot;</td>
<td>55</td>
</tr>
<tr>
<td>Si (mg/l)</td>
<td>ICP-AES</td>
<td>&quot;</td>
<td>&lt;10</td>
<td>&quot;</td>
<td>6.1</td>
</tr>
<tr>
<td>Cl⁻ (mg/l)</td>
<td>IC</td>
<td>&quot;</td>
<td>3300</td>
<td>&quot;</td>
<td>3700</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/l)</td>
<td>IC</td>
<td>&quot;</td>
<td>1400</td>
<td>&quot;</td>
<td>2100</td>
</tr>
<tr>
<td>HCO₃⁻ (mg/l)</td>
<td>Titration</td>
<td>0.05</td>
<td>140</td>
<td>0.1</td>
<td>110</td>
</tr>
<tr>
<td>Fe⁺⁺⁺ (mg/l)</td>
<td>Ferrozine</td>
<td>0.15</td>
<td>0.28</td>
<td>0.15</td>
<td>0.19</td>
</tr>
<tr>
<td>Fe₉₉₉ (mg/l)</td>
<td>Ferrozine</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>S(-II) (mg/l)</td>
<td>Spectrophotometer</td>
<td>0.15</td>
<td>&lt;0.1</td>
<td>0.15</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

n.a. = not analyzed

4.2 Titanium squeezing cell

In order to avoid changes in the porewater sample during squeezing, an improved squeezing cell was developed and tested. In the new cell, all the metal parts in contact with porewater were prepared of titanium to avoid the possibility to dissolve iron from the stainless steel into the solution or other reactions between the components in the solution and the metal surfaces. All the joints of the cell were sealed with o-rings and the syringe was fixed with glue to the cell in order to avoid leaking of gases.

The operation of the squeezing cell was tested with bentonite samples containing sulphide in the porewater. The bentonite used to prepare the samples was first kept in nitrogen flow in order to remove major oxygen and then moved into the anaerobic glove-box, where it was stored in an open bottle for three months. The compacted samples were prepared by mixing the oxygen-free bentonite with a certain amount of Åspö reference groundwater, to which some Na₂S was added. The sulphide concentrations in the solutions were 0, 10 and 20 mg/l. The bentonite-water mixture was then compacted to a dry density of 1.5 g/cm³. These samples were allowed to homogenize for three days in a glass bottle and then moved to the squeezing cells. The porewaters were squeezed out from the samples in five days. The solutions were moved out from the syringes and their S(-II) concentrations determined. It appeared that sulphide had completely disappeared from the squeezed porewaters. This straightforward test indicated that more accurate studies are needed.

The further tests included studies on the interactions of titanium, titanium sinter, stainless steel, stainless steel sinter, different o-ring materials, syringe materials and bentonite with sulphide solutions. The major findings of these tests can be summarized as follows:

- Titanium and titanium sinter do not essentially react with sulphide in dilute solution, but sulphide disappears in a few days from a saline water.
Stainless steel and the stainless steel sinter quickly remove sulphide completely from the solution.

- The o-ring materials NBR (Acrylonitrile-butadiene-rubber) and EPDM (Ethylene-propylene-diene-rubber) removed sulphide completely from the solution, while (Fluoro-rubber) FPM and PTFE (Poly-tetra-fluoro-ethylene) did not essentially react with sulphide.

- Glass syringes with a Teflon plug were tight, non-reactive, but too stiff. A simple syringe prepared of polyethylene and polypropylene appeared to be mobile and non-reactive enough to be used with sulphide solutions. Its tightness was acceptable although probably not the best possible, because there was no sealing in the plug.

- Bentonite itself appeared to react with sulphide. Because bentonite contains an abundance of dissolving sulphate, it was not possible to exclude the possibility of oxidation by analyzing the increase of sulphate in the solution. However, similar interaction tests with purified bentonite, from which sulphate was removed, indicated that sulphide is removed from the solution and not oxidized for sulphate. In a preliminary test, where 99 mg of MX-80 powder was dispersed in 22 ml of the reference porewater containing 35.5 mg/l sulphide, 76% of the sulphide was removed from the solution in four weeks. In a test where the volume of the solution was 5.5 ml and the concentration as above, all of sulphide disappeared. The capacity of bentonite to remove sulphide was about 6 mg of S(-II) per one gram of bentonite.

- Squeezing of bentonite caused damage in the cell walls and piston and the o-rings in the plug could not tighten the cell well enough. In order to make the cell tight from the direction of the piston, it had to be equipped with a separate shielding.

The final version of the advanced squeezing cell is presented in Figure 18. It is prepared of titanium, tightened with many o-rings of FPM, and covered with a shielding in order to avoid leaking from the direction of the piston. The sample is collected in a tight, non-reacting syringe.

![Figure 18. An advanced squeezing cell prepared of titanium.](image)

Because it was not possible to add sulphide into bentonite without reaction, an advanced testing method, which considered this reaction capacity, was used to test the squeezing
cell. About 5 g of bentonite powder was first mixed with Åspö reference groundwater (45 ml) containing enough sulphide (690 mg/l) to exhaust the reaction capacity of bentonite and leaving some extra sulphide in the solution. The decreasing of sulphide was analyzed as a function of time until a constant level was reached (Figure 19). The minor difference in the final sulphide concentration seen in the figure was caused by slightly varying bentonite-to-water ratios in those two samples. The bentonite was then separated from the solution and mixed with a certain amount of sulphide-free reference water in order to obtain a desirable final sulphide concentration in the solution. The bentonite was then separated from the mixture by centrifuging. The bentonite, still containing an abundance of water, was moved to the squeezing cell and the extra water was quickly squeezed away until the desired dry density (about 1.5 g/cm³) was obtained. The porewater of the compacted bentonite sample was then squeezed out in about one week. The sulphide concentrations of the solution squeezed out during the quick compaction and squeezed out during a week were analyzed. The results are presented in Figure 20.

![Figure 19](image_url)

**Figure 19.** Decreasing of sulphide concentration in the solution as a function of time in a water bentonite interaction experiment. Bentonite-to-water ratio was 5g/45 ml.

The behaviour of sulphide in the squeezing cell was tested without bentonite, too. Two millilitres of de-ionized water or the reference porewater containing sulphide was put into the squeezing cell. Half of the solution was left in the titanium cell, in the space where bentonite usually is, and the other half was squeezed in the syringe. After a week, sulphide concentrations in the samples taken from the cell and syringe were analyzed. The results of the test are presented in Table 7.
Figure 20. Testing of the advanced squeezing cell with bentonite samples saturated with sulphide containing reference water. Concentrations in the squeezed samples are presented as a function of total squeezed volume. The squeezing times of the fractions were 2, 4, 16, 44, 168 hours and 3, 9, 32, 168 hours for S1 and S2 respectively.

The test with the squeezing cell shows that reactions between sulphide and the titanium cell cannot be completely avoided. This concerns especially the solution of high salinity. In the syringe, sulphide stays quite well, however. While squeezing bentonite, the porewater is in contact with titanium through diffusion, which decreases the reaction rate. A direct contact with the titanium sinter is typically less than one day when the porewater flows from the cell to the syringe. It can be expected that the reaction is slow enough to allow squeezing without major changes.

Table 7. Changing of sulphide concentrations in the squeezing cell and syringe during a one-week test.

<table>
<thead>
<tr>
<th>Water type</th>
<th>Initial S²⁻ (mg/l)</th>
<th>In the syringe after 3 days S²⁻ (mg/l)</th>
<th>In the syringe after 7 days S²⁻ (mg/l)</th>
<th>In the Ti-cell after 3 days S²⁻ (mg/l)</th>
<th>In the Ti-cell after 7 days S²⁻ (mg/l)</th>
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</thead>
<tbody>
<tr>
<td>De-ionized water</td>
<td>3.9</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Åspö reference porewater</td>
<td>3.2</td>
<td>3.0</td>
<td>2.6</td>
<td>1.4</td>
<td>0.4</td>
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</table>
5 TRANSPORTATION VESSEL FOR THE BENTONITE SAMPLES

The bentonite samples, to be taken from the excavated parcels at the end of the experiment, have to be shielded against drying, oxidation and other possible changes caused by the surroundings during transportation and storing. Figure 20 presents the vessel constructed for that purpose. The vessel itself is prepared of stainless steel and the cover of aluminium. The cover is fixed with six bolts to the vessel and is tightened with an o-ring. Two valves in the cover are used to remove oxygen from the vessel by nitrogen flushing. The vessel is strong enough to be transported through a vacuum chamber into an anaerobic glove box. The tightness of the vessel was tested with gas overpressure where no leaking was noticed.

\[ C(t) = C_i + (C_0 - C_i)e^{-(Q/v)} \]  

(2)

where \( C(t) \) is oxygen concentration in the vessel, \( C_0 \) is oxygen concentration in the vessel at the beginning of flushing, \( C_i \) is oxygen concentration in the nitrogen and \( Q \) is the flow rate of the gas. Figure 21 gives the calculated concentration curves for oxygen, when the gas flow is 8 l/min, oxygen concentration in the nitrogen is 1 ppm and the free
volume of the vessel varies from 1 to 3 litres. The time needed for flushing is typically a few minutes. Flushing times that are too long have to be avoided because of the risk of drying the bentonite sample.

Shielding against oxidation was tested in different experimental arrangements with sulphide solutions. Open experimental tubes containing 10 ml of sulphide solution were closed in the transportation vessels in the anaerobic glove box. Two of the vessels were moved out of the glove-box into the normal atmosphere and two others stored in the glove-box. After three and seven days, the sulphide concentrations of the samples of each condition were analyzed. For comparison, open experimental tubes without any vessel were stored in the glove-box, as well. In one test, the volume of the solution was 200 ml in order to see the effect of the solution-to-vessel-volume ratio. In order to study the effect of the wall material of the vessel, experimental tubes containing 5 ml of the same solution were closed in glass bottles and in a plastic bottle of 2 litres.

Figure 22 gives the results for the tests. It is obvious that in all the conditions the sulphide concentration decreases. Further analyses of the solutions showed that the concentration of the total sulphur decreases in the same way. This means that sulphur moves as H₂S from the solution to the gas space of the vessel. The material of the wall
Figure 22. Decreasing of sulphide concentration in an open experimental tube (10 or 5 ml) or a bottle (200 ml) when stored in different conditions. Storing conditions: glove-box (box) and air. Vessel materials: no vessel (no), stainless steel (ss), glass bottle (gl), and plastic bottle (pl).

does not seem to have essential effect on the process. The concentration left in the solution increases when the volume of the solution is increased. In closed experimental tubes, sulphide stays without any problems. No oxidation of sulphur was found.

The oxidation was also tested with Fe$^{2+}$ solution. An open experimental tube of 10 ml was closed in the transportation vessel and stored in air for a week. The loss of Fe$^{2+}$ was about 5 %.

The tests show that oxidation can be avoided by closing the sample in the steel vessel in nitrogen atmosphere. A worse problem is the movement of H$_2$S from the sample to the free gas space of the vessel. To avoid this, the free space in the vessel and storing time should be minimized. The surface layer of bentonite should not be used in the studies, either.
6 SUMMARY

The Long-Term Test of Buffer Material (LOT) is underway in the Åspö Hard Rock Laboratory in Sweden. The testing principle is to emplace "parcels" containing a heater, central tube, pre-compacted clay buffer, instruments, and parameter-controlling equipment in vertical boreholes with a diameter of 300 mm and a depth of around 4 m. The temperature, total pressure, water pressure, and water content, are measured during the heating period. At termination of the tests, the water distribution in the clay is determined and subsequent well-defined chemical, mineralogical and physical testing are performed. The aim of the work described in this report was to develop and test methods for studies of the chemical properties of bentonite porewaters and bentonite itself.

Development work on the analyses comprised the selection of suitable methods for the most interesting chemical components and parameters in bentonite porewater. The selected methods were then tested with artificial samples considering the small sample size of 1 to 2 ml, which was assumed to be available. Most of the components of interest can be determined from a squeezed porewater sample by diluting the sample. ICP-AES appeared to be a suitable routine method for Na⁺, K⁺, Ca²⁺, Mg²⁺, Si⁴⁺ and ion chromatography (IC) for Cl⁻ and SO₄²⁻. In preliminary tests, the capillary electrophoresis appeared to be a promising method for Cl⁻, SO₄²⁻, Na⁺, Ca²⁺, Mg²⁺ in small samples, too. Analyzing silica and aluminium with atomic adsorption spectrophotometer with graphite oven techniques (GFAAS) was not successful. Sulphide could be determined with a spectroscopic method, and Fe²⁺ and Fe₄ox with the ferrozine method down to a level of 0.1 mg/l in the initial sample. Bicarbonate was determined by titration, the determination level being 1 mg/l in the initial sample.

In the study on pH measurement, the values obtained with a microelectrode (Orion Model 98-03) were compared with those obtained with a normal-size laboratory electrode. The test showed that a sample of 0.15 ml is big enough for the microelectrode to give reliable values.

In the study on Eh measurement, the values obtained with a microelectrode (Microelectrodes, Inc. Model MI-800-710) in a small and large sample were compared with those obtained with a normal-size laboratory electrode in a large sample. The solutions used in the measurements were reference porewaters to which different concentrations of S(-II) or Fe(II) were added in order to adjust Eh. The sample had to be closed carefully in the measurement cell to avoid oxidation or loss of H₂S. The values measured with the microelectrode in small and large samples match each other well, and the microelectrode gives comparable values with the normal-size electrode, too. A sample of 0.3 ml is enough for the microelectrode.

Measurement of the dissolved oxygen from diluted samples was tested with an analyzer of Orbisphere Laboratories. The method gave reliable values down to about 0.5 μg/l in the measured sample, but it is impossible to ensure that the sample remains unchanged for longer times.
The methods were also tested with porewater samples squeezed from bentonite samples. All the components of interest can be determined from a squeezed porewater sample of about 1.5 ml. Sulphide appeared to react with the many of the squeezing cell materials, however. To solve the problem, an advanced cell prepared from titanium, tightened with many o-rings and covered with a shielding in order to avoid penetration of oxygen into the cell was developed and tested. The test with the squeezing cell showed that reactions between sulphide and the titanium cell cannot be completely avoided but the reaction is slow enough to allow squeezing without major changes.

Testing work was carried out to find the reason for the changes of cation-exchange capacity (CEC) during different treatments of bentonite. It appeared that drying of bentonite by any method caused a decrease of 6-8 % in the CEC. In order to obtain comparable values, drying of all samples at 105 °C is proposed.

A vessel was constructed and tested for transportation of the bentonite samples to be taken from the LOT experiment. Shielding against oxidation was tested experimentally by closing S(-II) and Fe(II) solutions in open bottles in the transportation vessel. The tests showed that oxidation can be avoided by closing the sample in the steel vessel in nitrogen atmosphere. A worse problem is the movement of H₂S from the sample to the free gas space of the vessel. To avoid this the free space in the vessel and storing time should be minimized. The surface layer of bentonite should not be used in the studies, either.
REFERENCES


Comparison of added and measured concentrations determined by ICP-AES (cations) and ion chromatography (anions)

<table>
<thead>
<tr>
<th>Component</th>
<th>AP 1 (mg/l)</th>
<th>AP 2 (mg/l)</th>
<th>AP 3 (mg/l)</th>
<th>AP 4 (mg/l)</th>
<th>AP 5 (mg/l)</th>
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<td>31.7</td>
<td>106</td>
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Comparison of the added and measured concentrations by capillary electrophoresis

<table>
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<th>Component</th>
<th>AP 1 (mg/l)</th>
<th>AP 2 (mg/l)</th>
<th>AP 3 (mg/l)</th>
<th>AP 4 (mg/l)</th>
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<tr>
<td>K⁺ meas</td>
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<td>6.0</td>
<td>7.3</td>
<td>14.0</td>
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Procedure for bentonite porewater analysis

Conditions and preparative steps
To avoid oxidation of the redox-sensitive components, squeezing and handling of the porewater samples have to be carried out in an anaerobic glove-box where the oxygen concentration is < 2 ppm.

The pH and Eh electrodes have to be calibrated and tested with suitable test solutions in the anaerobic glove box to ensure their quick use. The electrodes, filling solutions and cells have to be kept in the glove box beforehand to remove oxygen from them.

All the reagents to be used for S(-II) and Fe(II) analyses have to be prepared and made oxygen-free. The methods have to be tested.

If possible, the size of the bentonite sample should be selected so that the volume of the squeezed porewater sample is > 1.5 ml. At the end of squeezing the sample is moved from the syringe into a centrifugal tube of 2.5 ml. The sample is centrifuged for 5 minutes at 10 000 rpm to separate possible particular material.

pH and Eh measurement
A sample of 0.3 ml is moved from the centrifugal tube to the pH/Eh measurement cell with a magnetic stirrer of 2 mm on the bottom. The pH is measured with a micro glass combination electrode (Orion Model 98-03) calibrated beforehand. To avoid changing of the sample the measurement should be carried out in a few minutes.

The pH electrode is replaced by an Eh electrode (Microelectrodes Inc., Model MI-800-710). The cell is carefully closed and the Eh readings recorded until the electrode is stabilized. Normally this takes from a few hours to one day. S(-II), Fe(II) and Fe_{tot} of the sample will be determined when the Eh measurement is completed.

Ultrafiltering
The rest of the sample in the centrifugal tube is moved into a centrifuge filter tube (Whatmann, Vectra Spin™ Micro, MWCO 12 k). The sample is filtered in order to remove traces of colloidal bentonite.

Determination of S(-II)
A sample of 0.2 ml is taken from the centrifugal tube and diluted to 3 ml with oxygen-free water. The reagents are added into the sample according the standard method (SFS 3038). The sample is taken out of the glove-box and measured in the spectrophotometer.

Determination of Fe(II)
A sample of 0.2 ml is taken from the centrifugal tube and diluted to 3 ml with oxygen-free water. The ferrozine reagent is added into the sample according to the method (Dimmock et al. 1979, Ruotsalainen et al. 1994). The sample is taken out of the glove-box and measured in a spectrophotometer.
**Determination of Fe_{tot}**
A sample of 0.2 ml is taken from the centrifugal tube and diluted to 3 ml with oxygen-free water. The sample is taken out of the glove-box. All of the iron in the sample is reduced for Fe(II) with tioglycolic acid and determined as Fe(II) (Dimmock et al. 1979, Ruotsalainen et al. 1994).

**ICP-AES and IC analyses**
The sample of 0.3 ml from the ultrafiltering is diluted to 5 ml and stored for ICP-AES and IC analyses. Further dilutions are made according the needs of the analysis method.

**Titration of HCO_{3}^{-}**
A sample of 0.3 ml from ultrafiltering is diluted with CO_{2}-free water to 5 ml and titrated to pH 4. HCO_{3}^{-} is determined on the basis of the Gran curve.