Technical Report
TR-16-14
July 2017

# Developing strategies for acquisition and control of bentonite for a high level radioactive waste repository

**Daniel Svensson**
**Christel Lundgren**
**Lars-Erik Johannesson**
**Karin Norrfors**

SVENSK KÄRNBRÄNSLEHANTERING AB

SWEDISH NUCLEAR FUEL
AND WASTE MANAGEMENT CO

Box 3091, SE-169 03 Solna
Phone +46 8 459 84 00
skb.se

SVENSK KÄRNBRÄNSLEHANTERING

ISSN 1404-0344
**SKB TR-16-14**
ID 1540673

July 2017

# Developing strategies for acquisition and control of bentonite for a high level radioactive waste repository

Daniel Svensson, Christel Lundgren, Lars-Erik Johannesson
Svensk Kärnbränslehantering AB

Karin Norrfors, ÅF

*Keywords:* Bentonite, Material control, KBP1009, XRD, CEC, XRF, Swelling pressure.

# Abstract

The report is a part of a stepwise development of methods and techniques for acquisition and quality control of bentonite in the future repository for spent nuclear fuel.

The technical requirements on the bentonite are quantified into a number of parameters i.e. swelling pressure, hydraulic conductivity and shear strength. This report describes the methods used for determine these parameters. Furthermore, measurements made with these methods are presented. Other test methods which are not related to any technical requirements but are important for describing the bentonite i.e. the water content, the bulk density, the granule size distribution and compaction properties are also presented.

The following methods were included in the report: cation exchange capacity (CEC), powder X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), exchangeable cations (EC), water content, bulk density, granule size distribution, swelling pressure, hydraulic conductivity, shear strength, compaction properties, analysis of carbon and sulphur and thermal conductivity. The common standard methods methylene blue and free swelling were identified as less suitable based on expected lower reproducibility or due to delivering less useful information, and were not included in the study.

The current requirements on the bentonite buffer and backfill are summarised and the current strategies for bentonite sourcing, screening, sampling, and quality assurance are briefly discussed.

The complementary use of X-ray diffraction (mineralogy), X-ray fluorescence (chemistry) and cation exchange capacity for characterisation is illustrated on a selection of Wyoming and Milos bentonite batches as delivered, and in the case of Wyoming also as when blended with sand, to simulate different buffer qualities and variations in the composition due to inhomogeneity of the delivery or due to contamination. It was found that an addition of 1 wt% of sand is around the limit of what is possible to detect with the current methods and a 5 % contamination is easily detected using XRF or XRD. Montmorillonite content as determined from XRD was compared to as determined from CEC, overall it was a fairly good agreement, but most likely the montmorillonite chemistry and CEC changed somewhat between the different shipments during the almost 20 years between the first and last one, introducing differences. Hence, when correlating bentonite properties to montmorillonite content, it is expected to be better to use a single batch of bentonite and dilute with milled sand to simulate different qualities instead of comparing different batches with minor differences in montmorillonite content.

For some of the investigated methods (e.g. XRD, XRF, CEC and EC) a milled bentonite material is recommended because it contributes to a more homogenous and more representative sample. It is important to keep in mind that long milling of bentonite material may affect the clay mineral properties. For other methods, such as swelling pressure and hydraulic conductivity milling is however not recommended as it may change the clay mineral properties.

A validation process was initiated for the cation exchange capacity method, and a number of tests were performed that illustrates the uncertainties of the method and the complexity of bentonite analysis in general; and although the method works very well, there are still several factors that are less well understood. The validation tests of the CEC method showed that the method has a high repeatability and within laboratory reproducibility standard deviation (2 %) for investigated matrices. The sample mass had a clear effect on the measured CEC, but the effect was very small in the vicinity of the mass selected in the method description. The Cu-tri solution buffered the pH and hence after the addition the type and amount of bentonite did not affect the pH of the solution. The dispersion time had no significant effect on the measured CEC, however, the reaction time had a clear impact, but the interval 10–100 minutes was very stable, which is suitable for laboratory conditions. In some cases, the CEC was affected by milling of the bentonite, but the results were inconclusive.

The uncertainties of the methods needs to be better quantified and compared to what is accepted. The current performance is expected by the authors to be good enough, but it remains to be demonstrated.

# Sammanfattning

Rapporten är en del av en stegvis utveckling av metoder och tekniker för inköp och kvalitetskontroll av bentonit vid det framtida slutförvaret för använt kärnbränsle.

De tekniska kraven på bentoniten kvantifieras i ett antal parametrar, ex svälltryck, hydraulisk konduktivitet och skjuvhållfasthet. I rapporten beskrivs de metoder som används för att bestämma dessa parametrar, och mätningar presenteras som är gjorda med metoderna. Andra testmetoder som inte är relaterade till tekniska krav, men är viktiga för att beskriva bentoniten i allmänhet inkluderas också, ex vattenhalten, skrymdensiteten, kornstorleksfördelningen och kompakteringsegenskaper. Följande metoder ingick i rapporten: katjonutbyteskapacitet (CEC), pulver röntgendiffraktion (XRD), röntgenfluorescensspektroskopi (XRF), utbytbara katjoner (EC), vattenhalt, skrymdensitet, kornstorleksfördelning, svälltryck, hydraulisk konduktivitet, skjuvhållfasthet, kompakteringsegenskaper, analys av kol och svavel och värmeledningsförmåga. Vissa standardmetoder så som metylenblått och fri svällning identifierades som mindre lämpliga baserat på lägre reproducerbarhet eller på grund av att de ger mindre användbar information, och ingick därför inte i studien.

De nuvarande kraven på bentonitbuffert och återfyllning sammanfattas och nuvarande strategier för bentonit inköp, provtagning och kvalitetssäkring diskuteras i korthet.

Kompletterande användning av röntgendiffraktion (mineralogi), röntgenfluorescens (kemi) och katjonutbyteskapacitet för karakterisering av bentonit illustreras på ett urval av Wyoming och Milos bentonit leveranser, och för Wyoming också när den blandats med sand, för att simulera olika buffert kvaliteter och variationer i sammansättningen på grund av inhomogenitet eller på grund av kontamination under transport. Det konstaterades att en tillsats av 1 vikt% av sand är runt gränsen för vad som är möjligt att detektera med de nuvarande metoderna och en förorening på 5 % kunde enkelt detekteras med XRF eller XRD. Montmorillonithalten bestämdes med XRD och med CEC, och det stämde i stort sett bra, men troligen har montmorillonitens kemi och CEC varierat något mellan de olika sändningarna under de ca 20 år som gått mellan första och sista leveransen. Därför, när bentonitens egenskaper ska korreleras med montmorillonithalt förväntas det att vara bättre att använda en enskild leverans och späda denna med mald sand för att simulera olika kvaliteter stället för att jämföra olika leveranser med små skillnader i montmorillonithalt som kan överskuggas av andra skillnader.

För vissa av de undersökta metoderna (t ex XRD, XRF, CEC och EG) rekommenderas en mald bentonit eftersom det bidrar till ett mer homogent och representativt prov. Det är viktigt att komma ihåg att långa maltider kan påverka lermineralet och dess egenskaper, och för vissa metoder som svälltryck och hydraulisk konduktivitet rekommenderas därför malning inte alls.

En valideringsprocess initierades för metoden katjonutbyteskapacitet, och ett antal tester utfördes som illustrerar komplexiteten av bentonitanalyser i allmänhet, och även om metoden fungerar mycket bra, finns det fortfarande flera faktorer som är mindre väl förstådda. Valideringstestet av CEC visade att metoden har en hög repeterbarhet och inom laboratoriereproducerbarhet hade en standardavvikelse på 2 % för undersökta matriser. Provmassan hade en tydlig effekt på den uppmätta CEC, men effekten var mycket liten i området av den utvalda provmassan som används i metoden. Cu-tri-lösningen buffrade pH-värdet och därmed hade typ och mängd av bentonit ingen påverkan på pH vid mätningen. Dispergeringstiden hade ingen signifikant effekt på den uppmätta CEC, däremot hade reaktionstiden en tydlig inverkan, men intervall 10–100 minuter var mycket stabilt, vilket är lämpligt för laboratorieförhållanden. I vissa fall påverkades CEC av malning av bentoniten, men resultaten var otydliga.

Osäkerheterna i metoderna behöver kvantifieras bättre och jämföras med vad som är acceptabelt. Den nuvarande prestandan förväntas av författarna vara tillräckligt bra, men det återstår att visas.

# Contents

# 1 Introduction

Bentonite is planned to be used as a barrier material in repositories for final disposal of highly radioactive spent nuclear fuel. The Swedish method for final disposal of spent nuclear fuel was developed by the Swedish Nuclear Fuel and Waste Management Co (SKB) and is denoted as KBS-3.

In the KBS-3 method (Figure 1-1) the radioactive waste (solid fuel pellets of mainly uraniumdioxide) is to be placed in a copper canister with a cast iron insert which is sealed by friction stir welding. The copper gives long-term chemical stability while the cast iron insert gives structural rigidity. The canisters will be placed at a depth of around 500 m in crystalline rock where the space between the canister and the rock will be filled with specially designed compacted bentonite blocks and pellets.

The most important properties of the bentonite are:

1. High swelling capacity, limiting the microbial activity in the deposition holes.
2. Low hydraulic conductivity, thereby minimizing any mass transport in the tunnels and deposition holes.
3. Appropriate plasticity to allow the buffer to keep the canister in position but also be flexible enough to limit the transfer of forces from movements in the surrounding rock.
4. Adequate long-term stability.
5. Sufficiently high thermal conductivity to ensure rapid heat transfer of the heat generated by the radioactive waste decay.
6. In the case of a broken canister the buffer should also slow down potentially escaping radionuclides by sorption, cation exchange or filtration mechanisms (Arthur et al. 2005).

Because of the slow decay, the radioactive waste is considered hazardous for a very long time (100 000 to 1 000 000 years). Therefore, we need to ensure that it is protected by the different barriers during this period, which puts high requirements on the buffer and backfill material and components; requirements which we need to ensure are met throughout the life of the repository. Karnland et al. (2006) characterised a diversity of different bentonites regarding the mineralogical and chemical content and geotechnical properties, and also verified the fundamental relation between the cation exchange capacity, the montmorillonite content and the montmorillonite layer charge. Additional bentonites were investigated in Svensson et al. (2011). On top of mineralogical, chemical and geotechnical investigations, also screening of the microbe populations in the bentonites and long term stability testing were performed. The long-term stability test was called the Alternative buffer material experiment and used accelerated heating conditions in a field test at the Äspö hard rock laboratory, Oskarshamn, Sweden.

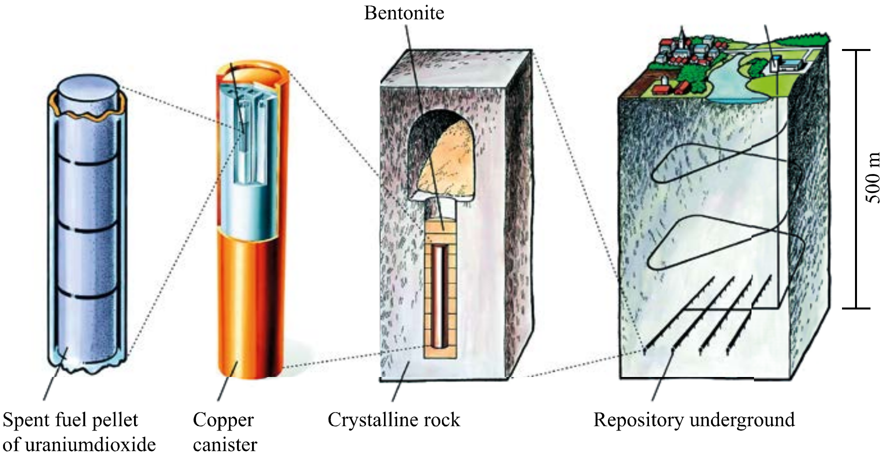

***Figure 1-1.*** *The protective barriers in the KBS-3 method of SKB (copper canister, bentonite clay, and crystalline rock) to keep the radioactive waste isolated from the environment. Buffer and tunnel backfill are made of pure bentonite clay.*

The amount of time available for performing the analysis in these studies was generally long and in general it was done by consultants that many times used various third party laboratory equipment at universities etc. However, for the future bentonite quality control, the delivered amount of bentonite will be much larger, the available amount of time much shorter, and it has to be performed by SKB personal with equipment mainly locally available. This report is a summary of a work conducted in order for SKB to be more self-reliant on material analysis of bentonite clay, regarding competence and laboratory infra structure, in order to be prepared for the future challenge of bentonite quality control at an industrial scale in the repositories for spent nuclear fuel and/or radioactive waste.

The word homogeneity is used in the report as a measure of how well blended the bentonite material is with regards to a specific property. An exceptionally homogenous material only needs to be sampled once, while a highly inhomogeneous material needs extensive sampling, blending and analysis.

## 1.1 Scope of the report

The report is a summary of a project conducted in order for SKB to be more self-reliant on material analysis of bentonite clay, regarding competence and laboratory infra structure. The report summarise the methods identified as critical or very useful for bentonite analysis, and for each method a standalone method description has been constructed.

The focus has been on the complex methods that need further development for SKB's application or on methods that are very easy to perform in an efficient way compared to using external laboratories. In contrast; there are analyses such as determination of carbon and sulphur where the analysis can be performed at low cost and with high quality and high speed at several international laboratories, and they were hence excluded from this work.

The requirements are summarised (Chapter 4); the current strategies for bentonite sourcing (Chapter 3), screening, sampling, and quality assurance are briefly discussed (Chapter 5–7).

The complementary use of X-ray diffraction (mineralogy), X-ray fluorescence (chemistry) and cation exchange capacity for characterisation is illustrated on a selection of Wyoming and Milos bentonite batches as delivered, and in the case of Wyoming also as when blended with sand, to simulate different buffer qualities and variations in composition.

One of the key methods, Cation exchange capacity, is investigated to a higher degree, and a number of tests were performed towards a validation of the method are included in the report in order to illustrate the uncertainties of the method and the complexity of bentonite analysis in general; and although the method works very well, there are still several factors that are less well understood.

# 2 Buffer and backfill

## 2.1 Bentonite as a raw material

*The following Section 2.1 was reproduced from Svensson (2015) with permission from the author.*

Bentonite is a swelling clay that consists of swelling clay minerals (smectites), normally montmorillonite, and various accessory minerals. A clay is defined as a naturally occurring material that is composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired (Bergaya et al. 2006). A mineral is defined as a naturally occurring (non-manmade) homogeneous solid with a well-defined chemical composition and crystal structure, and is usually formed by inorganic processes (Klein and Hurlbut 1998). Bergaya et al. (2006) listed various characteristics of clay minerals, but no stringent or non-ambiguous definition of a clay mineral is given.

Clay minerals are genetically either detrital allogenic minerals (transported residues from parent rock with no genetic relation to their present environment) or newly formed secondary or authigenic minerals formed in the sediment where the mineral was found.

Smectites are typically authigenic and are often formed by alteration of volcanic rock or by precipitation in alkaline continental basins (Bergaya et al. 2006).

The term bentonite comes from the clay formation at Fort Benton (Wyoming, USA) and bentonite comes in many colours (Figure 2-1 and Figure 2-2) and qualities. Bentonite is often found in layers with more or less of other layers of sediments on top, and hence in the commercial product, minor contributions from the other layers may also appear sporadically together with various contaminations.

***Figure 2-1.*** *Different colours of bentonite from Bavaria, Germany.*

***Figure 2-2.*** *Bentonite in Wyoming, USA. Notice how the colour changes in the different parts of the bentonite, which is generally interpreted as being due to differences in the Fe-redox chemistry in the bentonite.*

Smectites are layered silicates (phyllosilicates) which are structurally and chemically very similar to the macroscopic mineral mica. Although the difference in chemistry is quite small, the difference in some physical properties, such as swelling, is huge.

Stacks of smectite sheets are called tactoids, where each layer is randomly rotated on top of one another; this is called 'turbostratic disorder'. The smectite layers can be visualized with a transmission electron microscope (Figure 2-3), and although montmorillonite does not form macroscopic layers which can be seen by the eye, rectorite from Fort Sandeman in Pakistan does, and is perhaps the closest one can come to visually observing montmorillonite layers.

The Fort Sandeman rectorite is an ordered interstratification (super structure) of a swelling clay mineral (montmorillonite/beidellite) with a non-swelling clay mineral (illite/mica; Kodama 1966). In dry conditions, this material has a basal reflection (distance between each layer) of 24 Å (14 Å smectite + 10 Å illite/mica), and after liquid water has been added, the smectite component swells, whereas the illite/mica component remains unhydrated, giving the rectorite a basal spacing of 29 Å (19 Å smectite and 10 Å illite/mica).

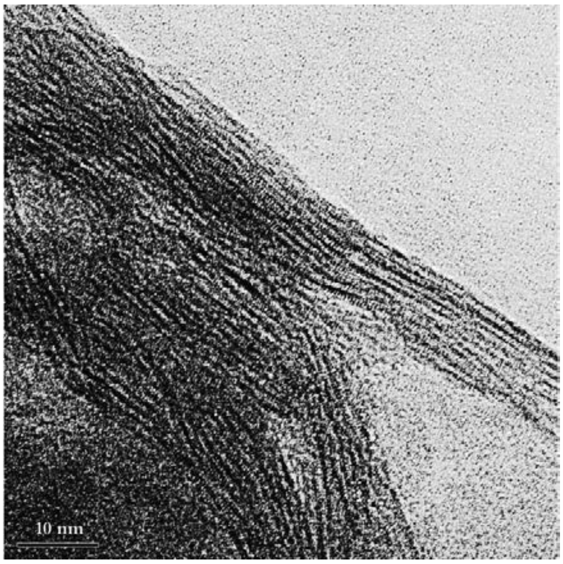

***Figure 2-3.*** *Transmission electron microscopy (TEM) micrograph of Na-montmorillonite (Wyoming) showing a platy texture. The scale bar is 10 nm. Image captured in collaboration with Reine Wallenberg, National Centre for High Resolution Electron Microscopy, Lund University.*

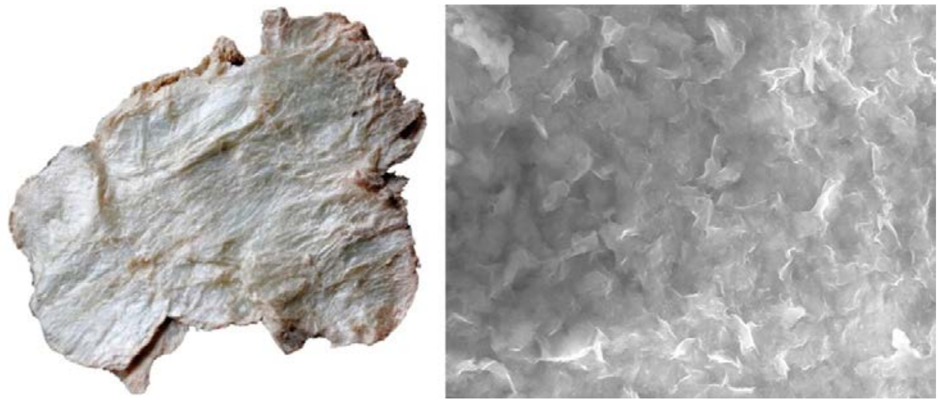

***Figure 2-4.*** *Left: rectorite from Fort Sandeman, Pakistan. Rectorite is an ordered interstratification of swelling and non-swelling clay minerals (specimen size: 47 × 35 mm) and is probably the closest one can come to looking macroscopically at montmorillonite. Right: TEM micrograph of Wyoming montmorillonite (image width ≈ 8 µm) showing its platy and wavy structures. Image captured in collaboration with Reine Wallenberg, National Center for High Resolution Electron Microscopy, Lund University.*

Different clay minerals often occur together as interstratified and/or separate phases. An estimation of the amount of illite in an illite-smectite interstratified clay can be made by swelling the sample with ethylene glycol (Moore and Reynolds 1997**).**

Clay minerals are divided into 1:1 layer clay minerals with one tetrahedral and one octahedral sheet (e.g. kaolinite and serpentine) and 2:1 layer clay minerals, with one octahedral sheet sandwiched between two tetrahedral sheets (e.g. pyrophyllite, talc, smectite, vermiculite, and illite). In montmorillonite the outer two sheets usually consist of silicon and aluminum (in corner sharing oxygen tetrahedra) and the middle sheet usually contains aluminum, magnesium and iron (in edge sharing oxygen octahedra).

Because of isomorphous substitutions in the crystal structure, each 2:1 layer has a negative charge (the most common substitutions are $Al^{3+} \rightarrow Mg^{2+}$ and $Si^{4+} \rightarrow Al^{3+}$). The size of this layer charge is what distinguishes smectites from other phyllosilicate minerals. If the layer charge were larger they would be approaching vermiculites and micas, and if it were absent, they would be pyrophyllite. In order to balance this negative layer charge, positively charged interlayer cations are situated between each layer (Figure 2-5c). The octahedral sheet of the smectite layer can contain three divalent metal ions per half unit cell (e.g. $Mg^{2+}$, $Fe^{2+}$, $Cu^{2+}$, $Zn^{2+}$) and is then called 'trioctahedral', or it can contain two trivalent metal ions (e.g. $Al^{3+}$, $Fe^{3+}$, $Cr^{3+}$) and is then called 'dioctahedral' **(**Moore and Reynolds 1997). The charge can originate from substitution either in the octahedral layer (e.g. dioctahedral montmorillonite and trioctahedral hectorite) or in the tetrahedral layer (e.g. dioctahedral beidellite, nontronite and trioctahedral saponite).

An example of a structural formula per unit cell (Figure 2-5) for a sodium saturated Wyoming montmorillonite is:

$Na_{0.65}(Al_{3.1,}\ Mg_{0.49,}\ Fe_{0.38,}\ Ti_{0.01})(Si_{7.89}Al_{0.11})O_{20}(OH)_4$ (Karnland et al. 2006).

Iron may be present as both Fe(II) and Fe(III) in the octahedral layer and is susceptible to redox reactions. If Fe(III) is reduced to Fe(II) this may impact the layer charge and hence some of the properties of the smectite (Stucki et al. 2002). The presence of several clay minerals (interstratified or not), accessory minerals, poorly crystallized or amorphous phases and sometimes also organic substances, can make analysis a challenge, especially if the stability of the sample is also taken into consideration.

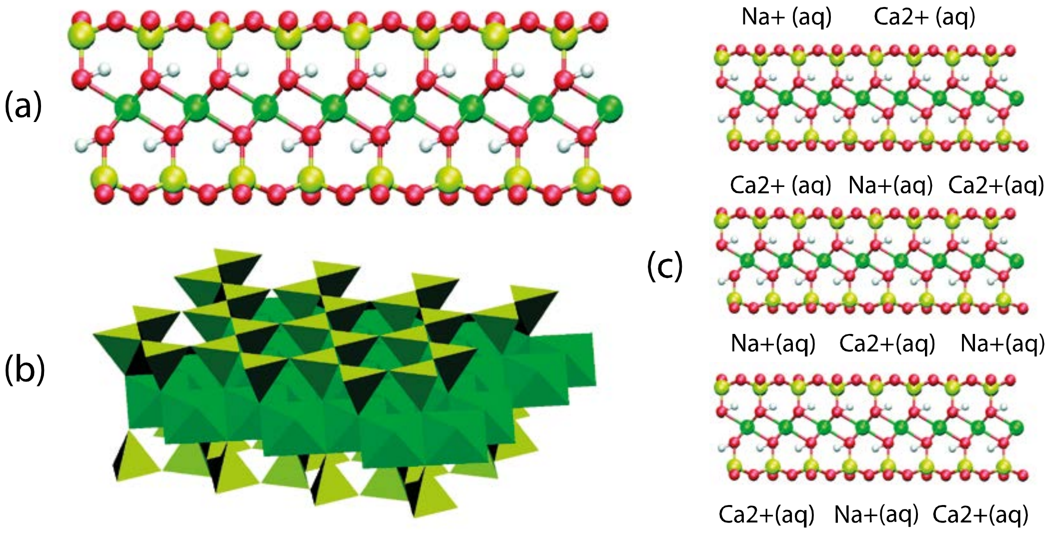

***Figure 2-5.*** *Illustration of the crystal structure of the smectite 2:1 layer as ball and stick representation (a), as polygon representation (b) and with* $Ca^{2+}$ *and* $Na^{+}$ *interlayer cations (c).*

## 2.2 Selection of methods

### 2.2.1 Motivation for selected methods

The methods selected as candidates for industrial quality control were selected based on the type of information they give, the quality of data with low uncertainties and little ambiguity, the relative ease of execution of the methods and maintenance of the equipment, with relatively high speed and as low usage of man hours as possible.

When selecting methods, the requirements are central, and they are presented in Chapter 4. Basically all of the requirements are tested with selected special methods directly. But most of the methods are far too slow and time consuming to test bentonite from every single deposition hole. Instead the composition of the clay is analysed for an averaged sample from every deposition hole. If the composition is constant, we assume the geotechnical properties will be to.

As shown in 2.1, the composition of the montmorillonite will affect its layer charge and properties. Hence the montmorillonite composition should be followed as it may change somewhat between shipments. This is done using the XRF method (Chapter 10) of the clay fraction.

The type of interlayer cations in the montmorillonite affect the short term swelling and water uptake properties and are tested with the exchangeable cations (EC) method.

The amount of montmorillonite in the bentonite will also affect the performance of the buffer components, and this will be studied for every single deposition hole using powder X-ray diffraction (Chapter 9) and Cation exchange capacity (Chapter 8). The bulk chemistry may also indirectly be used for montmorillonite content (as demonstrated in Chapter 20). The complementary use of X-ray diffraction (mineralogy), X-ray fluorescence (chemistry) and cation exchange capacity for characterisation of the bentonite content with focus on montmorillonite content is illustrated in Chapter 20 on a selection of Wyoming and Milos bentonite batches as delivered, and in the case of Wyoming also as when blended with sand. The sand is added to simulate different qualities of the bentonite and/or the effect from a contamination during transport.

The overall plans for quality assurance, the control strategy and material sampling are also very important when selecting the methods, as these will give information about how many samples to analyse and how much time that is available (Chapter 5 and 6).

Many other methods may be used sporadically as complementary techniques to solve various problems, the selected methods are the ones identified as standard methods for continuous in house use.

### 2.2.2 Methods not included

Traditionally a diversity of different methods is used for bentonite control. Some of the most common ones are free swelling, methylene blue test and various geotechnical tests such as cone test etc. These methods have not been included here as they either do not give direct information about any critical parameter, or the indirect information about the bentonite content and/or properties is of no or little value, or alternatively another method is expected to work better. The free swelling test gives information about the swelling volume of a specific amount of bentonite in water. The type of bentonite, the amount of montmorillonite, the type of interlayer cations and the salt content all will affect the result. Hence, the result will be very difficult to interpret. The methylene blue method is based on the ability of montmorillonite to absorb methylene blue. The exact relation between what in the montmorillonite that determines the amount absorbed is not trivial, the method is commonly performed by titration until a visual color change is observed. The Cu-tri CEC method is expected to be superior to the methylene blue method and is therefore chosen here. Although some methods are less usable they may nevertheless still be used as a complement in the future in the case a supplier is unable to use the more superior methods.

# 3 Sourcing of buffer and backfill

Bentonite occurs widely throughout the world. Resources are extremely large and are effectively limitless, according to *The Economics of Bentonite, 11th edition, 2008, Roskill Market Report.* (Roskill 2008)

In parallel, estimates done by Industrial Minerals in 2013, estimate the bentonite reserves to be more than 10 billion tonnes while the yearly production of bentonite is estimated to be 15–20 million tonnes.

Bentonite reserves are mainly distributed between China, the US, the CIS, Germany, Italy, Japan, Greece, Brazil, India and Turkey. Most of this bentonite is of the calcium variety; global sodium bentonite reserves are thought to be fewer than 500 Million tonnes.

**Table 3-1. World bentonite production by country in 2014, thousand tonnes.**

| | 2014 |
|---|---|
| United States | 4 660 |
| China | 3 600 |
| India | 1 450 |
| Greece | 1 000 |
| Mexico | 1 000 |
| Brazil, beneficiated | 500 |
| Japan | 500 |
| Turkey | 420 |
| Iran | 400 |
| Germany | 350 |
| Rest of the world | 3 720 |
| **Total** | **19 614** |

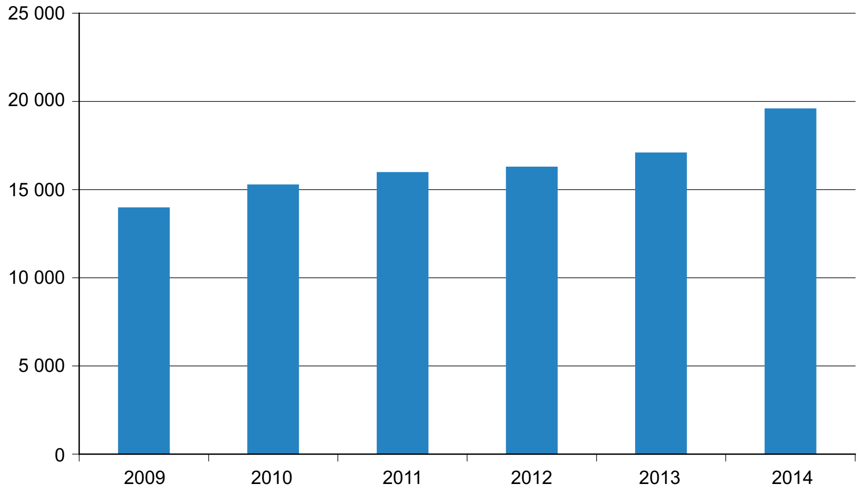

*Figure 3-1. Bentonite production dynamics in 2009–2014, thousand tonnes.*

The market for bentonite is mature and can be expected to grow in general relation to population growth.

The main suppliers of bentonite 2013/2014 were:

- AMCOL Specialty Minerals.
- S&B Minerals S.C.A.
- Bentonite Performance Minerals (Halliburton Energy Services).
- Asia Bentonite Co, Ltd.
- Ashapura Group.

## 3.1 Estimated volume of bentonite

SKB will use bentonite both for the buffer around the canisters in the KBS-3 concept and for the backfilling of the disposal galleries and main tunnels. The currently planned underground facility in Forsmark has a total volume of 2 940 000 $m^3$. The re-filling of this part of the facility will require more than 150 000 $m^3$ (255 000 tonnes) buffer-material for the disposal holes and 2 650 000 $m^3$ (4 500 000 tonnes) backfill-material.

## 3.2 Prices of bentonite

Bentonite is considered to be a classic "high-bulk low-value product" where the price of the product is more related to the transportation and handling costs rather than the cost of the actual material.

Example of prices for the bulk material delivered "Free-On-Board" according to the "Industrial Minerals Prices database in 2015:

- Price in January 2013 for Indian Bentonite, FOB Kandla, crushed and dried, loose in bulk, Civil Engineering grade was 32–40 $/tonne
- Price in January 2013 for Bentonite (dried material in bulk) FOB Greece: 65–75 EUR/tonne
- Price January 2013 for Bentonite, foundry grade crude and dried, bulk, FOB Milos: 60–80 EUR/tonne

In addition to the prices listed above we also have received price estimates on Wyoming bentonite clay of 95 USD/tonne not including transports.

For long term cost estimates we can assume that the raw material cost for buffer material is approximately 60–100 USD per tonne while estimated backfill cost will be approximately 40 USD per tonne (excluding shipping and handling).

## 3.3 Cost of transport

Transportation of bentonite can be divided into three stages:

1) During mining, material processing and loading on delivery transports.
2) During delivery to SKB's material handling centre.
3) From the material handling centre to SKB's production facility.

We will in this study focus on the second point as most of the cost of transports are relating to the transport from the suppliers processing plant to SKB's material handling centre. These transports are expected to be done using bulk transport ships.

### *Maritime transports*

The cost of maritime transports is governed by factors like geography, shipment size, safety concerns and type of cargo. In addition to this; the cost also varies a lot over time as a result of available transport capacity and the amount of available cargo.

Based on the review by UNCTAD (2013) we are currently at a period in time where the costs of maritime transport is at very low levels, which needs to be taken into account when studying the estimated costs listed below.

While no decision is yet made in regards to the final location of SKB's material handling centre we have in this cost analysis assumed that it will be located in Hargshamn and that transports will be made using bulk transport ships to the material handling centre. Currently this harbour is limited to handling 10 000 ton bentonite bulk transports. There are however advanced plans for extending the capabilities of the harbour so that it will be able to handle ships of up to 40 000–55 000 tonnes.

### *India – Hargshamn*

One of the largest suppliers of Civil Engineering grade bentonite is India. Based on discussions with the Ashapura Group there is a good shipping harbour in Mundra able to handle large quantities of bentonite.

A cost analysis was then made in cooperation with Tore Ulff Chartering and www.SeaRates.com where two different shipping alternatives were studied for a bulk transport from Mundra to Hargshamn. Both alternatives are based on actual shipping rates in October 2015 and include additional fees for transporting the cargo past the African Horn and the Suez Canal. Not included are costs relating to taxes and unloading of the cargo.

**Table 3-2. Cost of transporting bentonite from India to Hargshamn using bulk transport ships. Current limitation in hargshamn is 9 000 tonnes. Expected limit in Hargshamn is estimated to 55 000 tonnes.**

| Transport costs from India to Hargshamn | USD/tonne |
|---|---|
| Mundras – Hargshamn (9 000 tonne bulk ship) | 55 |
| Mundras – Hargshamn (55 000 tonne bulk ship) | 19 |

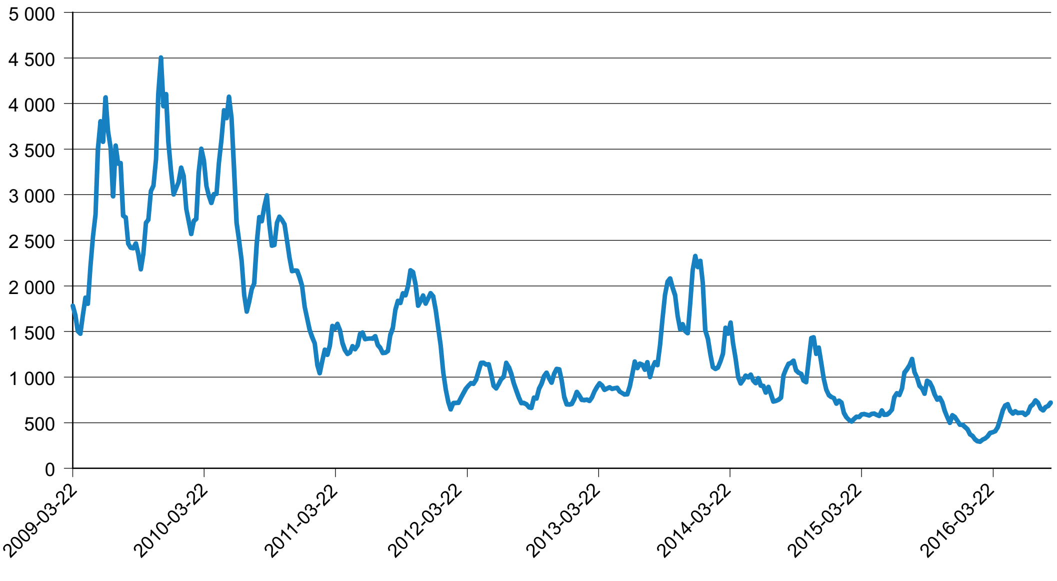

***Figure 3-2.*** *Baltic Exchange Dry Index, 2009–2016 (Index base year 1985 – 1 000 points) indicating world shipping costs. Highest point was in 2007 when the index was at an all-time high of 10 319 points indicating that cast of shipping was 10 times more expensive than in 1985.*

### *Greece – Hargshamn*

Large suppliers of bentonite are located around the Mediterranean sea where countries like Greece and Turkey are among the largest producers in the world. One of the suppliers in the area who supported SKB in our research has been Silver & Baryte Ores Mining Co. who are also the largest bentonite and perlite producer in Europe. One of their main harbours is located on the Greek island of Milos and they are there able to handle bulk transport ships with a capacity of up to 25 000 tonnes.

A cost analysis was then made in cooperation with Tore Ulff Chartering where two different shipping alternatives were studied for a bulk transport from Milos to Hargshamn. Both alternatives are based on actual shipping rates in October 2015. Not included are costs relating to taxes and unloading of the cargo.

**Table 3-3. Cost of transporting bentonite from the Mediterranean sea to Hargshamn using bulk transport ships. Current limitation in Hargshamn is 9 000 ton and 25 000 tons in Milos Harbour. Expected limit in Hargshamn is estimated to 55 000 tons.**

| Transport costs from Mediterranean sea to Hargshamn | USD/tonne |
|---|---|
| Milos – Hargshamn (9 000 tonne bulk ship) | 31.5 |
| Milos – Hargshamn (25 000 tonne bulk ship) | 15.8 |

### *USA – Hargshamn*

Most of the bentonite produced in the world is currently mined in the Wyoming area in the USA where, according to the Wyoming Mining Association, 3.7 Million tonnes of bentonite was produced in 2015.

The quality of the Wyoming bentonite is generally high and very even, but the transport costs are high for the Wyoming bentonite as it requires both train and boat transport.

Estimated transport costs are listed in Table 3-4. The bentonite material dedicated for the European market is, excluding local transport during mining and processing, transported by train cars to Port of Duluth where the materials are loaded to bulk ships. The size of the ships are limited to 21 000 tonnes because of limitations in the shipping lanes in the Great lakes.

**Table 3-4. Estimated shipping Costs for transporting bentonite from Wyoming to Hargshamn using train and bulk transport ships. Current limitation in Hargshamn is 9 000 ton and 21 000 tonnes in the shipping lanes on the great lakes. Expected limit in Hargshamn is estimated to 55 000 tonnes.**

| Estimated transport costs from Wyoming to Hargshamn | USD/tonne |
|---|---|
| Train transport Wyoming-Port of Duluth (bulk train cars) | 50 |
| Reloading costs at Deluth | 10 |
| Port of Duluth – Hargshamn (21 000 tonne bulk ship) | 45 |

## 3.4 Summary

SKB will source a total of approximately 4.7 million tonnes of bentonite material. The cost of the material can be estimated to over at least 200 million USD while necessary transports are estimated to cost 100 million USD. Clear plans and procurement specifications used during the procurement of the material is therefore of key importance.

The overall strategy should be that the quality of bentonite is assured already in the supply agreement process, for example by a QA-agreement that is also signed when the purchasing contract is signed.

# 4 Requirements

The requirements for a KBS-3 repository originate firstly from the principle that future generations should not be exposed to radiation doses larger than those currently accepted for nuclear facilities or activities, and secondly from the multi-barrier principle. According to the multi-barrier principle the post-closure radiation safety of a final repository shall be based on a system of passive barriers that act in different ways, either directly or indirectly by protecting other barriers in the system, so as to:

- isolate the repository from the surface environment,
- contain the radionuclides.

The requirements on each level of detail in the design provide specifications for a KBS-3 repository, individual barriers and barrier designs respectively. Figure 4-1 includes the criteria or terms used for evaluation of requirement conformity.

## 4.1 Buffer

A number of technical design requirements have been developed, that relates to the buffer safety functions (Table 4-1).

**Table 4-1. Buffer technical design requirements on properties and content (Posiva SKB 2017).**

| Characteristic | Technical design requirements | Safety function |
|---|---|---|
| Material specific relation between dry density and swelling pressure. | The minimum dry density yielding a swelling pressure > 3 MPa when determined with a specific laboratory test procedure. | Limit advective mass transfer.<br>Limit microbial activity.<br>Keep the canister in position. |
| | The maximum dry density yielding a swelling pressure < 10 MPa when determined with a specific laboratory test procedure. | Limit pressure on the canister. |
| Material specific relation dry density – hydraulic conductivity. | The minimum dry density yielding a hydraulic conductivity in saturated state < $10^{-12}$ m/s when determined with a specific laboratory test procedure. | Limit advective mass transfer. |
| Material specific relation between dry density and shear strength. | The maximum dry density yielding an unconfined compressive strength at failure < 4 MPa at a deformation rate of 0.8 %/min when determined with a specific laboratory test procedure, and for material specimens in contact with waters with less favourable characteristics than site-specific groundwater. | Mitigate the impact of rock shear on the canister. |
| Material composition. | The content of organic carbon shall be less than 1 wt-%. | Compatibility and reliability of production. |
| | The sulphide content shall not exceed 0.5 wt% of the total mass, corresponding to approximately 1 wt% of pyrite. | |
| | The total sulphur content (including the sulphide) shall not exceed 1 wt%. | |
| Thermal conductivity. | The thermal conductivity over the installed buffer shall, given the allowed decay power in the canister, the thermal properties of the canister and the rock and the canister spacing, yield a buffer temperature < 100 C°. | Long term stability.<br>Resist transformation. |

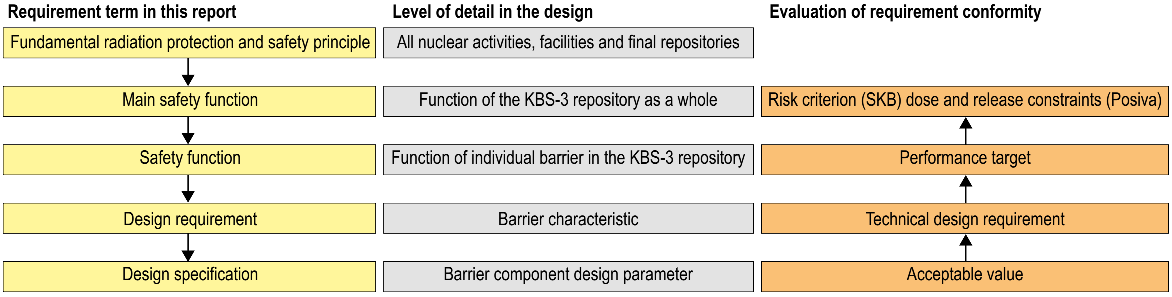

***Figure 4-1.** Relations between requirement terms used in this report, level of detail in the design and evaluation of requirement conformity.*

## 4.2 Backfill

The backfill and plug system shall contribute to these main safety functions of a KBS-3 repository by maintaining the safety functions to:

- keep the buffer in place and,
- limit advective mass transfer.

A number of technical design requirements have been constructed that relates to the backfill safety functions (Table 4-2).

**Table 4-2. Backfill technical design requirements (Posiva SKB 2017).**

| Characteristic | Technical design requirement | Safety function |
|---|---|---|
| Material-specific relation between dry density and swelling pressure. | An acceptable dry density is one giving a swelling pressure > 1 MPa when determined with a specific laboratory test. | Limit advective mass transfer. |
| Material-specific relation between dry density and hydraulic conductivity. | The minimum dry density yielding a hydraulic conductivity < $10^{-10}$ m/s when determined with a specific laboratory test. | Limit advective transport. |
| Installed backfill material mass. | The installed backfill material mass shall, in average in the tunnel volume between two deposition holes, result in a dry density ≥ the least required material-specific dry density determined for the specific backfill material. | Keep the buffer in place.<br>Limit advective mass transfer. |
| Deformation properties. | The overall deformation of the installed backfill both in dry and saturated state shall resist the swelling pressure from the buffer and maintain the buffer swelling pressure > 2 MPa in average over the buffer volume. | Keep the buffer in place. |
| Material composition. | Impurities in the backfill shall not provide a significant source of sulphide, as this may corrode the copper canister. Sulphide limit to be determined. | Compatibility and reliability of production. |

## 4.3 Control parameters

Based on the design premises there is a need to identify what control parameters we will use for the quality assurance. Most of the control parameters are direct measures of design parameters (organic carbon, sulphide and total sulphur, swelling pressure and hydraulic conductivity), but other control parameters are general measures of the material composition regarding chemistry and mineralogy to assure homogeneity of the bentonite batch.

In addition to measurements aimed at verifying the fulfilment of the design requirements we also need to develop a complementary characterisation process. This process will primarily be used during the characterisation of materials before/during procurement to compare different possible buffer and backfill material and possibly during the production to identify changes in the material, to validate that the variation in the material components are relatively low, as large changes in the material may have unforeseen consequences for the barrier long-term performance.

Montmorillonite is the active component in bentonite clay when it comes to swelling and sealing properties. Swelling and sealing measurements, e.g. swelling pressure and hydraulic conductivity, are important parts of a quality control of bentonite for a KBS-3 repository as there are specific demands on these properties for the bentonite to fulfil its safety functions. These experiments are, however, very time consuming and may not easily be applied at a very large scale in quality control procedures where many rapid analyses are also needed for continuous monitoring. If the mineralogy and chemistry is constant for a specific bentonite clay, the swelling pressure is also expected to be constant, if measured at the same density and if the same procedure is used with identical conditions such as temperature, salinity of external solution, sample size, etc. Hence, by analysing the mineralogy and chemistry of a number of representative samples of a bentonite batch, fewer samples are expected to be needed to be analysed when it comes to more time-consuming tests such as swelling pressure and hydraulic conductivity, as the important properties are regarded to be a function of the montmorillonite content.

# 5 Quality assurance and control strategy

The quality assurance process for bentonite described here covers sampling and analysis of the clay material used for the buffer and backfill in the KBS3-repository concept. The process for sampling and analysis is based on the ISO standard "Statistical aspects of sampling from bulk materials", part 1 and 2 (ISO 11648-1:2003), and ISO standard "Acceptance sampling plans and procedures for the inspection of bulk materials" (ISO 10725:2000) combined with the results from sampling routines and measurements performed at SKBs material science laboratory at Äspö.

The quality assurance and characterisation of bentonite will be performed during multiple stages in the procurement, manufacturing and installation process for the buffer and backfill where analysis will be performed. These stages are:

1. Initial bentonite characterisation – laboratory scale, used for material selection.
2. Compaction and homogeneity – full scale, used for material selection.
3. Receiving of material – industrial scale, for a selected material.
4. Production process, for a selected material.
5. Installation, for a selected material.

The quality assurance and characterisation of bentonite is presented below for each of the steps separately.

## 5.1 Initial bentonite characterisation – laboratory scale

Any bentonite material that is considered potentially interesting as either buffer or backfill material is first characterised at laboratory scale regarding the bentonite content and properties. This is initiated by SKB, requesting a small material sample to be sent by a number of suppliers to SKB's material science laboratory for characterisation. The amount of material is recommended to approximately 20–200 kg of raw bentonite material per material sample. Several different materials can be asked to be sent from one supplier if the supplier has the opportunity to deliver multiple varieties of bentonite.

The result of the investigation is a short report with data from analysis of the material's suitability as a buffer and/or backfill material. A basic supplier review and estimates of material costs including shipping should also be included in the report. After comparing the different bentonite candidates, decisions are taken regarding which bentonites and suppliers that will be chosen to proceed to the subsequent full scale material characterisation including compaction of full size bentonite blocks.

The parameters studied, and methods used, during this process are listed in Table 5-1. Additional methods may be needed to characterise the bentonite in a satisfactory way.

**Table 5-1. Suggested standard bentonite analysis.**

| Parameter | Method |
|---|---|
| Swelling pressure | Oedometer – Chapter 15 |
| Hydraulic conductivity | Oedometer – Chapter 15 |
| Mineral and chemical composition | XRD – Chapter 9<br>XRF – Chapter 10 |
| Cation exchange capacity | Cu-tri method – Chapter 8 |
| Compaction curve | Small scale compaction – Chapter 17 |
| Thermal conductivity | ASTM D5334-08 – Chapter 19 |
| Sulphur content | Chapter 18 |
| Sulphide content | Chapter 18 |
| Organic carbon content | Chapter 18 |
| Water content | Oven drying and weighing – Chapter 12 |

## 5.2 Compaction and homogeneity – full scale

The first step before buying a bentonite shipment is to choose a smaller group of possible suppliers based on the results from the initial characterisation process (5.1). The chosen suppliers are contacted and a larger representative sample of bentonite is ordered (approximately 10 tonnes) which will be used for an extended large scale characterisation, including compaction of full scale blocks.

During this step the raw material homogeneity (mineralogy, chemistry), and production of full scale buffer/backfill components, will be tested. A minimum of three full scale ring blocks are produced and analysed in regards to density distribution, distribution of water content and 3-point bending tests.

The parameters studied, and methods used, during the large-scale characterisation are listed in Table 5-2.

**Table 5-2. Suggested parameters for extended characterisation of buffer and backfill materials.**

| Parameter | Method |
|---|---|
| Homogeneity of content and properties | Selected analysis from Table 5-1 (Table 5-1) |
| Granule size distribution | Sieving and weighing – Chapter 0 |
| Tensile strength | Beam test or Splitting tensile test |
| Mechanical stability of pellets | Shaking and sifting |
| Shear strength | Uniaxial compression tests |
| Dry density blocks | Chapter 0 |
| Dry density pellets | Chapter 0 |

The result of the extended characterisation is an extensive report with both data from the analysis, comparisons to material previously used for the barriers and results from analysis of the materials suitability as a buffer and/or backfill material. Included in the material report will also be (1) material specific design parameters (min/max-levels, as well as nominal values and their acceptable variations for different parameters, etc.) that ensure that the functional requirements (see Posiva SKB 2017) can be met, (2) description of how the material may vary in mineral composition to still be considered as the characterised bentonite material and thereby fulfil the specific design parameters which are described in (1) to verify the functional requirements, and (3) material specific requirement specification to be used during the request for the full material shipment. In addition, the requirement specification will list the methods that will be used for the verification of the requirements.

## 5.3 Receiving of material – industrial scale

The bentonite material will be shipped to SKB's material handling centre, preliminary located in Hargshamn, using bulk transport ships. The estimated size of individual shipments will be between 10 000–40 000 tonnes with a total estimated quantity of 65 000 tonnes of raw material per year on average.

Quality assurance will be performed during the actual receiving of the bulk-transported material. The quality assurance will only verify that the material specific requirement specification is fulfilled and if the full delivery can be accepted. Bentonite samples will be taken at given time intervals from the conveyor belt used for unloading the cargo. These samples will be analysed as presented in Table 5-3 and compared to the specific requirement specification used during the request for tender for the full material shipment. Samples for detecting the swelling pressure and hydraulic conductivity will be taken together with the other samples during the sampling process, but analysed later due to the longer time required for analysis. However, these results have to be approved for the bentonite batch before transporting the material to the production buildings.

The result of analysis performed during receiving of material is a letter of acceptance including verification that the material specific requirement specification has been met. SKB has then confirmed that the delivered full material shipment is the material that SKB was ordering.

The parameters studied will vary depending on the material but is expected to include parameters and methods listed in Table 5-3.

**Table 5-3. Suggested parameters studied during the receiving of bentonite at industrial scale.**

| Parameter | Method |
|---|---|
| Selected bentonite analysis, excluding compaction curve and thermal conductivity. | Selection from Table 5-1 Table 5-1 (excluding compaction curve and thermal conductivity). |
| Large contaminants. | Visual inspection at the grate of the crusher. |
| Radioactivity. | Gamma detector. |

## 5.4 Production process

The production process includes all the process steps from the time that the material is transported from the primary storage at the material handling centre to the local crusher and drier, transported to the production facilities and finally production of buffer or backfill blocks and pellets. A number of quality assurance measurements are performed throughout the process with the goal to ensure the quality of the buffer and backfill components produced before actual installation.

Measurements are performed both on samples collected after the crushing and drying at the material handling centre, and on samples collected before mixing the actual process material used in components produced. The produced blocks are measured to control their dimensions and weighted to determine their density. Also, a given volume of pellets is weighted to determine the density of the pellets. If the buffer blocks are machined to the desired dimensions after swelling for several days after production, the blocks will be measured and weighed once more after processing. In the end of the production line, all buffer and backfill blocks will undergo visual inspection for detection of larger cracks as a last control in the production process. All the parameters studied and the methods used are listed in Table 5-4.

There is an ability to conduct an extensive sampling during the production process if needed to assure that the quality of the production is high. This is especially important when for example a new bentonite material is chosen as the raw material for the process.

**Table 5-4. Suggested parameters to be studied during the production of buffer and backfill components.**

| Parameter | Method |
|---|---|
| A selection of the standard bentonite analysis | Selections of Table 5-1 |
| Granule size distribution | Sieving and weighing |
| Mechanical stability of pellets | Shaking and sifting |
| Block dimensions | Laser measurement |
| Pellets dimensions | Manual measurements |
| Dry density blocks | Chapter 0 |
| Dry density pellets | Chapter 0 |
| Block appearance | Visual inspection of colour, cracks, corners etc |

## 5.5 Installation process

The installation process includes all the process steps from the time that the buffer and backfill components are placed in the interim storage until the components are installed in the deposition hole or used for the backfilling of a tunnel section. The methods for controlling and measuring blocks and pellets during the installation process controls are important to be able to verify the function of the installed barriers.

During the installation process, measurements of the deposition hole as well as the backfill tunnel will be performed to control if installation of the barriers is possible. The position (both horizontally and vertically) of the buffer blocks will be controlled during installation of the buffer. The stacking pattern of the backfill block will be controlled and the block fill ratio will be reported as well. Finally, the amount of installed pellets (both for the buffer and backfill) will be measured to estimate the total installed density for the buffer and backfill, respectively.

All the parameters measured and the methods used during the installation process are listed in Table 5-5.

**Table 5-5. Parameters studied during the production of buffer and backfill components.**

| Parameter | Method | Acceptance criteria | Comment |
|---|---|---|---|
| Block dimensions. | Laser measurement. | **Buffer, compact:**<br>Height: 540 mm<br>Diameter: 1 650 mm<br>**Buffer, rings:**<br>Height: 477 mm<br>Diameter: 1 650 mm<br>**Backfill:**<br>400 x 571 x 500 mm | Exact measurements are reported.<br>Construction requirements.<br>Installation requirements. |
| Dry density blocks. | Chapter 13. | Acceptance criteria is identified during characterisation. | **Buffer:** One value per block is reported.<br>**Backfill:** Mean value and StDev are reported.<br>Fulfilment of the requirements of swelling pressure. |
| Dry density pellets. | Weighing a given volume incl. water content determination. | Acceptance criteria is identified during characterisation. | Mean value and StDev are reported.<br>Fulfilment of the requirements of swelling pressure. |
| Block appearance. | Visual inspection of colour, cracks, corner qualities etc. | Acceptance criteria is identified during production. | Ok/Not ok is reported.<br>Manageability of block. |

# 6 Material sampling at different scales

The sampling process is dependent on the pre-treatment of the material. Hence, the sampling procedure differs between the different steps in the production chain for buffer and backfill. The amount of bentonite present at the sampling occasion and the time frame of sampling define the possible numbers of samples for each occasion. The containers where the bentonite is stored at the sampling occasion are also affecting the sampling procedure since sampling with a sampling spear can be used while the bentonite is transported in e.g. big bags, whereas sampling from a conveyor belt should be performed at receiving of material due to the large quantity of bentonite. An illustration of the production process for the buffer and backfill material is presented in Figure 6-1.

In this section, all parameters which are important for the sampling procedures during the different stages (laboratory scale, full scale, industrial scale and installation) are presented. When the information is of general character, the parameters are presented under a general subsection and valid for all sampling occasions. However, when the sampling procedure is specific for the production step, the information is presented for each subsection, respectively.

## 6.1 Definition of sub-lots

A batch sample of bulk material has to be divided into sub-lots where at least one sample has to be sampled from each sub-lot. According to ISO 11648-1:2003 at least 20 samples should be taken from a batch to be able to significantly characterise the batch. However, in cases where sampling will be carried out when the bentonite is placed in silos or big-bags, at least one sample must be taken from each silo.

### *Initial bentonite characterisation – laboratory scale*

When receiving e.g. a 20 kg sample from the suppliers, each kg can be defined as a sub-lot. Therefore, sampling on each kg should be performed. Each sub-lot may be analysed and/or sub-lots may be combined into a composite sample for analysis.

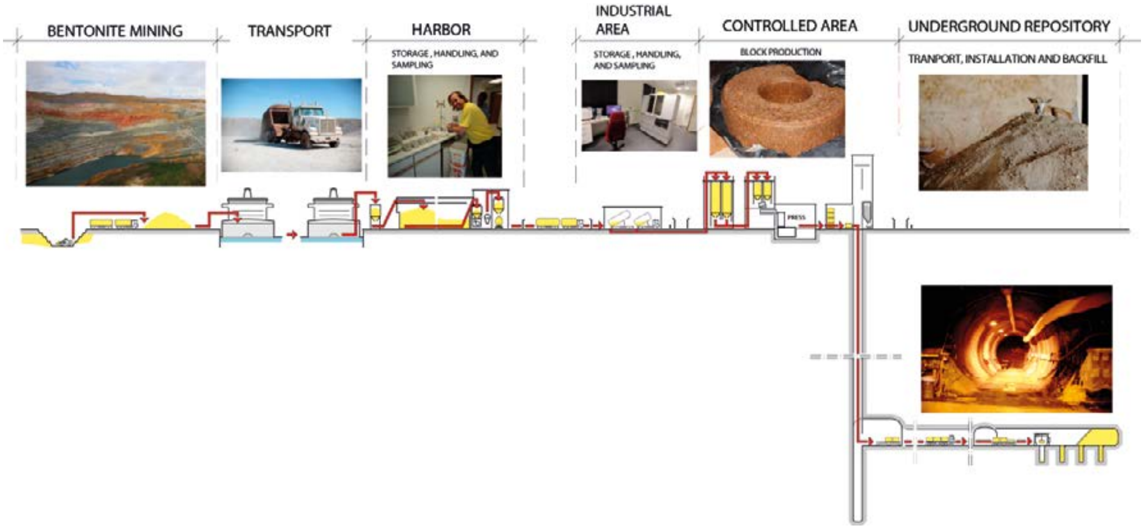

***Figure 6-1.*** *Schematic illustration of the bentonite flow from the mine to the repository, with several possible check points for material sampling and control. The pictures were taken from existing bentonite applications and are not intended to give detailed information about the production process, but were added as a visual aid.*

### Compaction and homogeneity – full scale

The material obtained for the full-scale characterisation will most likely be delivered in bags of approx. 1 tonne/bag. Therefore, each of the delivered bags should be defined as one sub-lot and sampling from each bag should be performed. Each sub-lot may be analysed and/or sub-lots may be combined into a composite sample for analysis.

### Receiving of material – industrial scale

When receiving the full delivery of bentonite, the sub-lots are defined by the time of unloading from the ship. The total amount of bentonite should be divided in 20 sub-lots and include the amount of bentonite unloaded during 1/20 of the total time of unloading the cargo. This is explained in more detail in Section 6.8. Each sub-lot may be analysed and/or sub-lots may be combined into a composite sample for analysis.

### Production process

The production process is a continuous process and sampling should be performed continuously when needed. However, all buffer/backfill components produced during one working shift can be defined as a sub-lot.

### Installation

During installation, one deposition hole or one tunnel section (approx. 6 meters) is defined as sub-lots, respectively.

## 6.2 Particle properties

Depending on the particle size distribution of the material in the batch the sampling must be adapted.

The particle properties which affect the needed amounts (mass) of each sample for analyses are *the nominal top size* (i.e. the particle size which corresponds to the smallest particle size of the 5 % largest particles in the bulk material) and *the particle density*. These properties give the minimum cutter aperture width required to avoid bias where a mechanical sampler is used, or the minimum size of the ladle required to avoid bias where manual sampling is used. For montmorillonite (which is the major part of bentonite), the particle density is found to be:

**Particle density of montmorillonite:** $2.75–2.78 \times 10^3$ kg/m$^3$ (Komine and Ogata 2004)

However, the nominal top size of the bentonite differs for the samples depending on how the bentonite is pre-treated in the production chain. The nominal top sizes for each production step are therefore presented in the subsections below.

### Initial bentonite characterisation – laboratory scale

The bentonite material received is crushed and sieved at the supplier to the requested grain size, but not further crushed at SKB. Therefore, the nominal top size of the samples is estimated to:

**Nominal top size:** 10 mm

### Compaction and homogeneity – full scale

When receiving the full scale delivery of bentonite material, the bentonite is crushed and sieved at the supplier to the requested grain size, but not further crushed at SKB. Therefore, the nominal top size of the samples is estimated to:

**Nominal top size:** 10 mm (Arvidsson et al. 2015)

### *Production process – industrial scale*

During the production process, the bentonite has been pre-treated at SKB by crushing the material to a granule size distribution optimal for production of blocks and pellets. Therefore, the nominal top size of the samples is estimated to:

**Nominal top size:** 5 mm

### *Installation*

No sampling will be performed on bentonite particles during the installation steps. Therefore, no nominal top size is given in this production step.

## 6.3 Sampling procedure

This section describes how the sampling procedure is planned to be performed for the buffer and backfill. Generally, any system where the bentonite is present must be clean so that samples are not contaminated. If a bentonite sample becomes contaminated, the chosen value for the design parameters and verification of the design may be based on incorrect analysis results. For the same reason, storage of samples must not affect analysis results due to contamination. Sample preparation should be performed in the same way for all samples for a specific analysis so that no sample preparation can affect the results and so that measurements can be compared between different samples.

## 6.4 Sampling equipment and place for sampling

The location of sampling should be chosen according to the following criteria:

- ensure that consideration is given to the safety of operators,
- ensure the sample cutters are located at a point which affords access to the complete bulk material stream,
- perform sampling at a point in the handling system where there is no apparent visual segregation of the material stream and where there is no apparent risk of errors due to a periodic variation in material feed or quality regarding e.g. particle size distribution or water content,
- perform sampling as closely as possible to the loading or unloading point where the quality characteristics are to be determined, for example close to the place of receiving the bentonite material or the place where the quality of the bentonite will be characterised.

When conducting sampling, the sample should be taken in one single motion by moving the ladle, scoop or manual sampling spade at a constant rate through/over the entire width of the bulk material stream. Also, alternative samples can be taken by moving the sampling bucket through the bulk material stream in the opposite direction so that sampling error can be excluded from the analysis results. When using a bucket, face the bucket upside down and move the bucket through the bulk material flow to the other side. Turn the bucket upright again and move the bucket back through the flow (ISO 10725:2000). Alternatively, the bucket can be filled by passing through the bentonite stream once, from front to back, provided that it can then be withdrawn from the flow.

The sampling equipment must be designed so that it can manage to take the relevant amounts of samples of bentonite particles with the characteristics listed in Section 6.2. The equipment should also be designed so that the probability of taking a sample is the same everywhere in the entire amount of bentonite. In manual sampling, the paddle with which sampling is performed, a volume of at least $3d \times 3d \times 3d$, is needed. The minimum mass that the paddle has to sustain is then:

$$m_l = 27 \times \rho \times d^3 \times 10^{-6} \qquad (6\text{-}1)$$

where $m_l$ is the mass, expressed in kilograms, of the increment; $\rho$ is the bulk density of the material, expressed in tonnes per cubic metre and $d$ is the nominal top size, expressed in millimetres, of the particles of the material. The minimum volume and mass required for sampling is presented in the subsection of each production step below.

#### *Initial bentonite characterisation – laboratory scale*

Sampling should be performed on a carefully homogenised 20-kg bag and the aim is to take samples from each kg in the bag. The minimum volume and mass required during sampling is 27 $cm^3$ and 75 g when using the particle properties presented in Section 6.2.

#### *Compaction and homogeneity – full scale*

At full scale material characterisation the bentonite will be transported in big bags or silos/containers. When the bentonite is placed in the container, a sampling spear should be used for sampling where a sample is taken in a carefully homogenised container. The sampling should be performed at least 20 cm into or in the centre of the container.

#### *Receiving of material – industrial scale*

The full-sized delivery of bentonite will be unloaded from the ship on a conveyor belt. Sampling should therefore be carried out on the bentonite flow at the conveyor belt for optimum distribution of the samples at specific time intervals. The speed of the conveyor belt must be even and the conveyor belt must be able to transport bentonite without segregating it by size.

The minimum volume and mass required during sampling is 27 $cm^3$ and 75 g when using the particle properties presented in Section 6.2.

#### *Production process*

Sampling and measurements will be performed continuously during production of blocks and pellets. Therefore, testing/analysis will be performed on all the produced block, filled pellet silos and continuous measurements should be placed on the flow of raw materials. Measurement systems should alarm when deviations in measurements are detected.

The minimum volume and mass required during sampling is 3.4 $cm^3$ and 9.3 g when using the particle properties presented in Section 6.2.

#### *Installation*

Monitoring of the installation steps will take place continuously and automatically during the installation. Measurements for determining the installation quality, i.e. measuring stacking pattern for installed backfill block, positions for installed buffer block and amount of pellets installed, will be performed by the installation machines.

No bentonite particles will be sampled for analysis during installation, whereas no minimum volume and mass is presented for this production step.

## 6.5 Number of measurements on each sample

The number of samples is determined by the number of sub-lots of the bentonite batch, as defined in Section 6.1. One sample should be taken from each sub-lot and, where it is possible, the sample is divided into an A- and a B-sample to be analysed separately. A mean value of the A and B sample can then be estimated with its standard deviation.

## 6.6 Variabilities

During sampling, variabilities between measurements should be calculated so that systematic errors that can occur during sampling are detected and, if present, the implementation of the sampling can be changed. Depending on where in the sampling process the variability is highest, the variability from the analysis results can be lowered by increasing the number of samples, by decreasing the uncertainties during performing the sampling or by choosing an analyst instrument with lower uncertainties. An example of how the variability can be calculated for all measured values ($s_{Iunc}{}^2$) of the total amount of bentonite is:

$$s_{Iunc}^2 = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2 \tag{6-2}$$

where $n$ is the number of increments, $x_i$ is the value of the quality characteristic (i.e. the result from the analysis) for increment $i$ and $\bar{x}$ is the average of the quality characteristic measured on all increments.

## 6.7 Minimum sampling amount

The mass of the sample must be large enough so that the sample can be used in all analyses planned, incl. extra material so that new samples for analyses can be prepared if the samples get destroyed during sample preparation. In Section 6.4 the minimum sample mass corresponding to the minimum sample volume was calculated for each production step. However, a larger sample quantity will be required to be able to carry out to all the planned analyses.

### *Initial bentonite characterisation – laboratory scale*

Most of the 25 kg-batch will most likely be used for sampling during screening of material. The aim is that each kg will be sampled to be analysed by all methods presented in Table 5-1.

### *Compaction and homogeneity – full scale*

When the bentonite is placed in silos at least 1 kg bentonite should be taken as a sample from each silo for further analysis.

### *Receiving of material – industrial scale*

Upon receiving of material, 10 ± 0.1 kg bentonite should be the mass of a sample which is sampled from a conveyor belt. This mass of 10 kg should be shaken and afterwards 1 ± 0.05 kg should be taken from the 10 kg-sample for preparation for analysis.

### *Production process*

During the production process, samples are taken in such quantity required for measurements to be carried out. In cases where the measurements have a supervisory function (when no destructive testing is required, for example XRF, measurements of block, weighing) all the raw materials, all produced blocks and all silos with pellets will be tested. The required sample quantity needed for each analysis is presented in the method descriptions.

### *Installation*

During installation, the measurements performed have a supervisory function whereas all blocks and the whole volume of installed pellets will be measured to assure high quality of the installation process.

## 6.8 Sampling interval

The sampling interval should be so that the minimum amount of required samples can be sampled evenly distributed over the total amount of bentonite, which is specific for each of the production steps for the buffer and backfill. Therefore, the sampling interval for each production step is presented in the subsections below. The minimum amount of required samples is 20 samples if not defined otherwise.

### *Initial bentonite characterisation – laboratory scale*

The sampling interval during screening of material should be so that samples from each kg in the 25 kg-batch can be taken and analysed.

### *Compaction and homogeneity – full scale*

The sampling interval during material characterisation should be so that samples from every bentonite silo can be taken and analysed.

### *Receiving of material – industrial scale*

Sampling interval during receiving of material should be such that the minimum number of samples ($n$) can be carried out so that they are evenly distributed over the total amount of bentonite ($m_{tot}$). The sampling interval can be set at either time ($\Delta t$) or mass basis ($\Delta m$). This is illustrated by the following equations:

$$\Delta m = \frac{m_{tot}}{n} \tag{6-3}$$

alternatively,

$$\Delta t = \frac{m_{tot} \cdot b}{n} \tag{6-4}$$

where $b$ is the mass flow of bentonite on the conveyor belt.

The first sampling should be performed within $< \Delta t$, alternatively $< \Delta m$, starting from the moment that the unloading of bentonite starts. The following sampling should take place with a fixed time or mass range.

The bentonite will be unloaded on a conveyor belt and the mass flow of bentonite on the conveyor belt must be determined. Thereafter, $\Delta t$ can be determined for which sampling should take place $n$ numbers of times. $n$ is defined in Section 6.1 as the minimum number of sub-lots for the bentonite.

### *Production process*

For testing of blocks and pellets in silos the sampling interval should be of the length that sampling can be performed on each block and each pellet silo.

### *Installation*

The sampling interval for the installation process is depending on the installation rate. During all installation steps, measurements will be performed and reported.

# 7 The samples in the laboratory

The sampling strategy must correlate to the question in mind. If the variation between the bentonite bags is to be investigated a representative sample of each bag must be taken. Other targets could be to investigate the variation within a bag, or to see differences between different batches or between different mines/clay formations. This chapter is a summary of practical work performed at Äspö during the period of this project.

## 7.1 Sampling

Very little work has been done so far on this step at SKB. One shipment (MX80 BÅT 2015) was sampled using sample spears that took vertical samples in the big bags. It took some time and required some rather hard physical work. An alternative to sample spears that has been used at SKB is to remove the upper part of the clay and to collect bentonite further down in the bag. The variations in the MX80 2015 batch seemed to be too small to show a difference between a blended sample from many bags compared to a single sample, however this was not extensively tested.

## 7.2 Milling

Bulk sample of the different matrices have been milled prior to analysis, using a ball mill (Retsch PM400) with grinding jars of zirconium oxide or stainless steel (Figure 7-1). The samples were dried in the oven at about 40 °C before milling to become less plastic. Milled bulk samples are more homogenous, which contributes to a reduction of the spread of the measurements, but long milling may affect the clay mineral properties (e.g. CEC). Typically 200 rpm is used for 5–10 minutes.

## 7.3 Preparation of purified homoionic smectite

When the bulk bentonite is studied, it is sometimes necessary to purify and study the montmorillonite by itself. The presence of impurities, such as carbonates, hydroxides/oxides, organic and amorphous material of a clay mineral, can influence the identification and structural formula determining the clay mineral. By producing a purified fine fraction (particles with spherical diameter < 0.5 microns) these impurities can be excluded. Clay minerals can contain different amounts of these impurities. Depending on the clay fraction to be purified purification steps and the extent of these steps may differ. It may take various chemical and physical treatments to remove these impurities. However, these treatments can affect the structure of the clay mineral and often a balance must be made depending on the clay minerals to be studied and the purpose of the study (Bergaya et. al 2006).

***Figure 7-1.*** *Ball mill equipment. Right: Different inserts for ball mill of zirconiumoxide and stainless steel. To the right of the table the compaction mold for the XRF samples can be seen.*

In this work the focus has been on three steps in the purification process to obtain a fine fraction of clay mineral:

1) Ion exchange of clay to the $Na^+$ form with sodium chloride.
2) Separation of fine fraction through fractionation or centrifugation according to Stokes law.
3) Dialysis of fine fraction with dialysis membrane (Spectrapore 3, 3500 MWCO), to remove excess of salt.

Sodium and calcium montmorillonite swell differently, and in order for a smectite to be dispersed successfully it must contain a certain number of sodium cations in the interlayer. This may be done by cation exchange through repeated washing (3×) using 1 M solutions (0.1 M is enough for divalent cations; Moore and Reynolds 1997). After cation exchange the salt is removed by washing with water followed by dialysis. To separate the clay fraction (e.g. < 0.5 µm particles) sedimentation is used, as large particles sediment faster than smaller ones. This is described by Stoke's law (Moore and Reynolds 1997):

$$V_T = g\,(d_p - d_l)D^2/18\eta \qquad (7\text{-}1)$$

where $V_T$ is the velocity of sedimentation, g is the force of gravity (9.82 m/s$^2$), $d_p - d_l$ is the difference in density of the particle and the liquid, $D$ is the particle diameter and η is the viscosity of the liquid η. The time needed for a specific particle size to sediment to a specific depth can be calculated as $t = h/V_T$, where h is the distance (depth). To speed things up, a centrifuge is normally used. After the separation the clay fraction (e.g. < 0.5 µm diameter size) is obtained.

***Figure 7-2.*** *Purification of clay fraction using dialysis to remove salts. This is a very slow process that normally takes some weeks.*

# 8 Cation exchange capacity (CEC)

## 8.1 Introduction

The CEC of the bulk bentonite divided by the CEC of the pure montmorillonite give a good indication about the montmorillonite content of the bentonite and is a very good complement to other methods such as XRD. The method is fairly quick and normally easy to interpret, but differences in the sample preparation and in the method itself can, if they are not well controlled, reduce the reproducibility of the method.

The specific cation exchange capacity (CEC) of a bentonite depends on the number of cation exchangers in the clay and the specific cation exchange capacity of the smectite itself in terms of charge per gram. The exchangeable cations are compensating two types of negative charges in the smectite; (1) permanent charge from layer (isomorphous) substitution, (2) variable edge charges depending on the pH. If the CEC of the smectite is known, the bulk CEC of a bentonite is a good measure of the smectite content, as long as no other cation exchangers are present.

The CEC can be determined in several ways. One method is to extract the cations with an $NH_4Cl$ (or $NH_4OAc$) solution. Analysis of the extract gives information regarding the type and number of the cations present. One disadvantage with this method is that dissolvable phases (e.g. gypsum) also contribute to the result. This can however be minimized with an 80 % ethanol solution instead of water (Belyayeva 1967). Another method is to exchange with a $Cu^{2+}$ – triethylenetetramine complex (Meier and Kahr 1999). As the Cu-tri complex has a very strong blue colour this reaction can be rapidly quantified by using spectrophotometry. The exchange reaction is fast and is normally completed in 15 to 30 minutes (Figure 8-1). The measured CEC on pure montmorillonite correspond very well to the calculated layer charge on Wyoming montmorillonite based on chemical composition (Karnland et al. 2006) hence it is very well established that $Cu^{2+}$ is absorbed as a divalent cation in amounts corresponding to the permanent charge. The ratio of the CEC of the bulk bentonite and the clay fraction normally correspond very well to the montmorillonite content determined by methods such as XRD (Karnland et al. 2006) indicating that no other significant cation exchangers are present. The complementary use of X-ray diffraction (mineralogy), X-ray fluorescence (chemistry) and cation exchange capacity for characterisation is illustrated in Chapter 20 on a selection of Wyoming and Milos bentonite batches as delivered, and in the case of Wyoming also as when blended with sand.

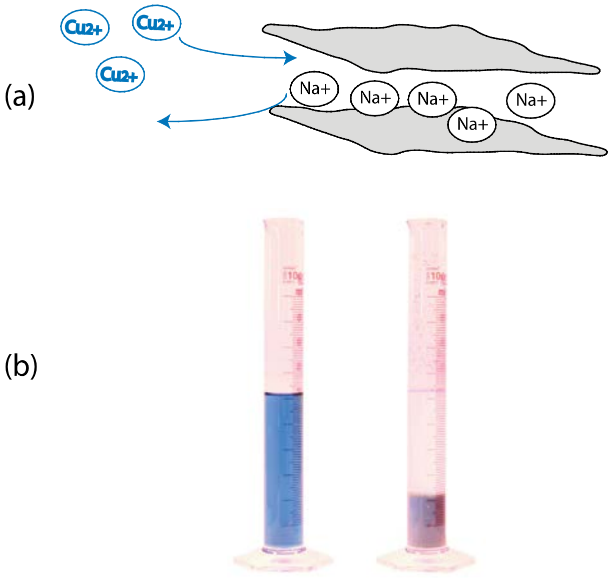

***Figure 8-1.*** *(a) Schematic illustration of the cation exchange reaction of Na+ to Cu2+ in montmorillonite (b) The cylinder to the left contains a pure solution of a Cu2+ complex. In the cylinder to the right, sodium dominated bentonite (MX-80) has been added and mixed with the solution. Decolouring of the solution finished in approximately ten minutes.*

### Method

The copper triethylenetetramine (Cu-tri) method was investigated and adapted (amount of sample and concentration of solution) for laboratory operation for CEC determination of smectite rich bentonites. The method determines the total CEC (permanent layer charge and variable edge charge) and is based on Meier and Kahr (1999) and Ammann et al. (2005). The principle for determining the CEC by copper-tri method is to disperse the bentonite in deionised water and then equilibrating with copper (II) solution. The exchange is rapid and complete after about 30 minutes (Ammann et al. 2005). Because hydrated copper (II) has a very strong blue colour, this may easily be measured and quantified by spectrophotometry. CEC is calculated by the difference in the copper concentration before and after ion exchange with the clay and are reported as the mean CEC of two separate determinations expressed as centimol charge, cmol(+)/kg dry weight.

### Interferences and sources of errors

The amount of bentonite sampled for one CEC determination is small (< 0.5 g). This makes it difficult to take a representative sample if the bulk material is not homogenous, e.g. large aggregates. Therefore milled bentonite is preferred when considering sampling a homogenous bulk sample for CEC determination. However, it is important to verify that the milling procedure (e.g. milling time, material of the grinding jars and balls) doesn't have an unwanted effect on the bentonite and hence CEC, see Section 7.2.

As the CEC are reported in relation to the dry weight of a bentonite sample, water content of the material must also be determined. It is essential that the weighing of bentonite for CEC and water content determination is carried out at the same time and under the same conditions, see Chapter 12.

If the bentonite has a large content of organic material this can result in a false high CEC (vanLoon and Duffy 2000). It is therefore important to storage the samples under conditions that prevent organic material to grow in the bentonite. The absorption coefficient of copper (II) solution is pH dependent, i.e. the capacity of $Cu(tri)^{2+}$-complex to absorb light is affected by pH. At lower pH, there is a protonation of the complex formed and the absorption coefficient decreases. Additionally, smectite minerals have higher charge at high pH values due to deprotonation of the hydroxyl groups. Depending on the pH of the samples after copper (II) solution have been added, samples might be buffered that a pH ≥ 8 is obtained (Ammann et al. 2005).

## 8.2 Analytical procedure

Bulk bentonites are milled 10 minutes at 200 rpm prior to analysis, using a ball mill (Retsch PM400) with grinding jars of zirconium oxide. Before milling, the samples are dried in an oven at about 40 °C to become less plastic.

### Calibration

A standard solution of 45 mmol/l copper triethylenetetramine is used for preparing calibration solutions of 2.97; 5.04; 7.02; and 9.00 mmol $Cu^{2+}$/l. The absorbance of the calibration solutions and a "zero sample" (deionised water) are measured spectrophotometrically at 583 nm (absorption maximum) in a 10 mm cuvette. The measuring is performed as duplicates and against water as blank. By plotting copper concentrations against measured absorbance, the equation of the calibration curve is calculated by linear regression (8-1). The equation is then used to estimate unknown $Cu^{2+}$ concentration of test samples.

$$y = kx + m \tag{8-1}$$

where

| | |
|---|---|
| $y$ | absorbance |
| $k$ | slope of the curve |
| $x$ | $Cu^{2+}$ concentration (mmol/l) |
| $m$ | y-intercept i.e. the value of y when the line crosses the y axis |

### *CEC determination*

Milled bentonite (400 mg ± 10 mg) is dispersed in 33 ml deionised water on a vibrating table for 30 minutes and then undergoes ultrasonic treatment for about 15 minutes. The bentonite is then equilibrating with copper (II) solution adding 7 ml 45 mmol/l Cu (II)-triethylenetetramine and placed on a vibrating table for at least 30 minutes. Triethylenetetramine which is an organic ligand is added to the copper (II) solution to enable the exchange and to avoid precipitation of unwanted copper complex. The organic ligand is added to the copper (II) solution with 10 % excess. After 5 minutes of centrifugation at 3 000 RCF (relative centrifugal force) spectrophotometer measurements at 583 nm are performed, using a double-beam spectrophotometer (Schimadzu UV2600), with 1 cm quartz cuvettes. The measurements are performed against a calibration curve. The CEC of test sample is calculated according to equation 8-2 to 8-5. The measuring range is 1–9 mmol/l $Cu^{2+}$ and the method is used for bentonites with a CEC of about 40–100 cmol(+)/kg dry weight.

Dry sample mass ($m_{\mathrm{dry}}$) is calculated as follows:

$$m_{\mathrm{dry}} = m_{\mathrm{undried}} \times (1 - wc/100) \tag{8-2}$$

where

| | |
|---|---|
| $m_{\mathrm{dry}}$ | dry sample mass (g) |
| $m_{\mathrm{undried}}$ | undried sample mass (g) |
| $wc$ | water content (%) |

Added molar amount $Cu^{2+}$ ($n_{\mathrm{addedCu2+}}$) to the bentonite is calculated as follows:

$$n_{\mathrm{addedCu2+}} = (C \times V) \times 1\,000 \tag{8-3}$$

where

| | |
|---|---|
| $n_{\mathrm{addedCu2+}}$ | molar amount $Cu^{2+}$ added (mmol) |
| $C$ | $Cu^{2+}$ concentration of the Cu-tri solution (mmol/l) |
| $V$ | Added volume of the Cu-tri solution (ml) |

The $Cu^{2+}$ uptake ($n_{\mathrm{uptakeCu2+}}$) of the bentonite is calculated as the difference of the added molar amount $Cu^{2+}$ ($n_{\mathrm{addedCu2+}}$) and the measured amount $Cu^{2+}$ ($C_{\mathrm{measuredCu2+}}$).

$$n_{\mathrm{uptakeCu2+}} = n_{\mathrm{addedCu2+}} - ((C_{\mathrm{measuredCu2+}} - C_{\mathrm{blank}}) \times V) \tag{8-4}$$

where

| | |
|---|---|
| $n_{\mathrm{uptakeCu2+}}$ | $Cu^{2+}$ uptake of the bentonite (mmol) |
| $n_{\mathrm{addedCu2+}}$ | molar amount $Cu^{2+}$ added (mmol) |
| $C_{\mathrm{measuredCu2+}}$ | measured $Cu^{2+}$ concentration (mmol/l) |
| $C_{\mathrm{blank}}$ | blank concentration (mmol/l) |
| $V$ | sample volume (liter, l) |

As $Cu^{2+}$ is divalent the CEC is counted as 2 number of mole of Cu per kg dry clay:

$$CEC = (1\,000 \times n_{\mathrm{uptakeCu2+}} \times 2)/(1\,000 \times m_{\mathrm{dry}}) \times 100 \tag{8-5}$$

where

| | |
|---|---|
| $CEC$ | cation exchange capacity (cmol(+)/kg dry weight) |
| $n_{\mathrm{uptakeCu2+}}$ | $Cu^{2+}$ uptake of the bentonite (mmol) |
| $m_{\mathrm{dry}}$ | dry sample mass (g) |

CEC is calculated by the difference in the copper concentration before and after ion exchange with the clay and are reported as the mean CEC of two separate determinations (i.e. mean CEC of two separate samples) expressed as cmol(+)/kg dry weight. As the CEC are reported in relation to the dry weight of a bentonite sample the water content of the material must also be determined. The water content is determined by weighing the sample before and after oven drying at 105 °C for 24 hours. The water content is reported in weight percent, see Chapter 12.

### *Method uncertainty*

An estimation of the expanded uncertainty of the Cu-tri method has been carried out in accordance with methodology described by Örnemark (2001). Possible sources of uncertainty in the analytical method have been listed (e.g. sample weighing, preparation of copper (II) solution, preparation of calibration curve) and individually tested for standard uncertainty. Combining these uncertainties together with repeatability and within laboratory reproducibility of control samples, reference samples and real samples an expanded uncertainty has been estimated to ± 8 % using a coverage factor of 2 to achieve about 95 % confidence. This estimated expanded uncertainty is based on CEC data corrected for the dry weight of the samples.

Control samples consist of copper triethylenetetramine solution with different concentrations within the calibration range. Reference samples consist of milled Wyoming bentonite (MX80) batches dated 2012. Real samples are samples of different batches of MX80, Ibeco and Asha bentonites. All these samples have been analysed as duplicates. No certified reference material has been available for these tests. To estimate the bias of the Cu-tri method additional test with certified reference material should be performed.

# 9 Mineralogy – powder X-ray diffraction (XRD)

## 9.1 Introduction

The XRD method gives crystalline phase composition of the bentonite, in other words the mineralogy of the clay. The method is relatively time consuming due to sample preparation, long measurement time and sometimes difficult to evaluate. Differences in the sample preparation and in the data evaluation have a relatively large impact on the results and may reduce the reproducibility of the method. The results however, give a very good picture of the mineralogical content of the bentonite, qualitatively and quantitatively, when properly done, information that cannot easily be gathered with any other technique.

The minimum amount of sample can be as low as about 20 mg for a highly crystalline powder when measured on a zero background silicon holder, while for a bentonite clay about 3 grams is needed when using a backfilled sample holder. As the method is non-destructive the powder can later be used for other analysis, e.g. XRF if needed. A highly crystalline sample can be measured in about 5–10 minutes while a bentonite sample normally requires between 1–3 hours. A system found to be very good for bentonite analysis is a system with a 2-dimensional detector, cobalt broad focus X-ray tube, no monochromator and a programmable divergency slit (Figure 9-1). The 2-dimensional detector decreases the measurement time by a factor of 10–100X compared to a single point detector, but may potentially affect the resolution and/or shape of minor details in the diffractogram. With bentonite it is difficult to get a high signal to noise ratio (due to the low crystallinity of clay minerals) and at the same time keep the measurement time reasonably low. Hence some sacrifices needs to be done. The same reasoning was done with the choice of no monochromator. The X-ray tube produces Co K-alfa and K-beta radiation, the K-beta radiation is not wanted. The monochromator selects a very thin wavelength span and hence increases the resolution, but at the same time decreases the X-ray flow (intensity), and hence increases the measurement time if used. The programmable divergency slit opens up at high angles to increase the signal/noise ratio at high angles, but still allows the slit to be small at low angles. If using a big slit at low angles parts of the direct X-ray beam may hit the detector and will affect background shape and resolution. Standard with XRD is to use copper X-ray tube, however, samples high in iron will give rise to fluorescence when Cu K-alfa is used. As many bentonite samples are high in iron, a cobalt tube was selected to avoid this. To reduce the Co K-beta flux a thin iron foil was used as a filter between the X-ray source and the sample.

***Figure 9-1.*** *X-ray diffraction equipment at Äspö clay science laboratory. The microscope is used for sample preparation.*

X-ray diffraction in crystals is called Bragg diffraction and is a consequence of the scattering of coherent X-rays (preferably monochromatic) from the electron clouds surrounding the atoms, and how these scattered photons (waves) interfere with each other through constructive and destructive interference in the crystal structure. Hence, depending on the types of atoms (higher atomic number = more electrons and higher scattering ability) in the structure and their internal geometric relations, different resulting waves will exit the crystal and can be recorded as scattering maxima at different angles in relation to the incident beam. The scattering can be visualized as X-ray scattering from different lattice planes within the crystal structure (Figure 9-2), and the relation between the scattering maxima and interplanar distances is described by Bragg's law (Atkins 1998):

$$\lambda = 2d_{hkl} \sin \theta_{hkl} \tag{9-1}$$

where $\lambda$ is the wavelength, d is the distance between planes *hkl* (Miller index defining the plane) giving rise to the diffraction maxima, and $\theta$ is half of the angle between the incident and the diffracted beam. A scattering maximum occurs when the X-rays are in phase and constructively interfere with each other. This is the case when the difference in travel path is equivalent to the wavelength, or in other words the distance ABC = $\lambda$. The distance AB = d sin $\theta$, and because AB = BC and ABC = 2 AB one can see that ABC = $\lambda = 2d_{hkl} \sin \theta_{hkl}$. For a fixed wavelength, each maximum corresponds to an interplanar distance in the crystal structure. A monochromator can be constructed similarly by keeping the crystal fixed and different wavelengths will thus scatter at different angles which can be separated by a slit. The width of the diffraction peak is a function of the sample particle size and is described by the Scherrer equation (Patterson 1939). Very small particles such as clay minerals give rise to broader peaks, whereas larger crystals give rise to narrower peaks. This is one factor in why clay minerals have broader reflections than most accessory minerals such as quartz, another is the high variability in the composition. The letter d correspond to an interplanar distance and can be expressed more specifically as $d_{hkl}$ for the interplanar distance between the hkl planes.

## 9.2 Analytical procedure

XRD data can be collected in transmission mode or in reflection mode. The equipment used in this project is used in reflection mode only.

Different types of samples can be measured. In this project a bulk sample in random orientation has been analysed. Additionally other preparation techniques can be used and will be evaluated further in the future, most important are (1) adding an internal standard such as corundum with a known

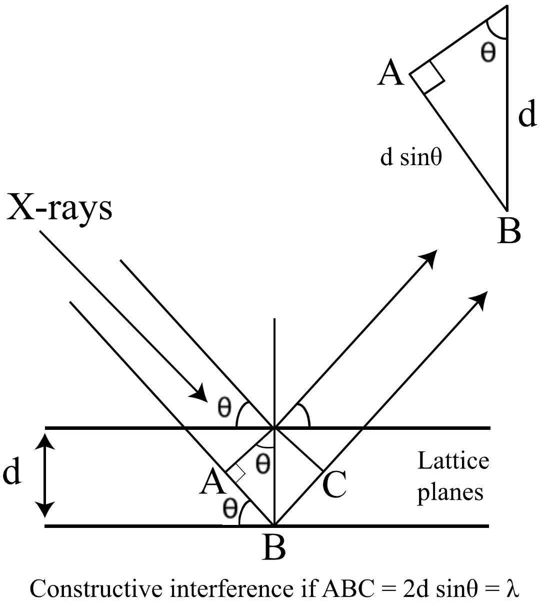

***Figure 9-2.*** *Schematic illustration of Bragg's law describing X-ray diffraction maxima (λ is the wavelength).*

amount in wt% to quantify the amorphous content, and (2) to measure the clay fraction as an oriented mount in air dry and ethylene glycol saturated state to evaluate the clay mineralogy in further detail. Due to the platy nature of montmorillonite it is difficult or even almost impossible to prepare a perfectly randomly oriented sample with bentonite. Slight orientation can be corrected for by the software, but it is important when comparing samples that they have been prepared as similarly as possible.

Evaluation of the bulk powder data can be done qualitatively or quantitatively depending on the purpose of the investigation. Of course, correct qualitative evaluation is an essential start for quantifying the data. The data in this project have been evaluated by the Siroquant rietveld software. A rietveld software is a computer code that will model a theoretical XRD dataset and compare it to, and iteratively refine it towards the observed dataset. The number of parameters that can be refined is rather huge, and in order to make the refinement work, things have to be refined more or less in a specific order. The user has to have an understanding of the physical meaning of the parameters in order to judge what is reasonable or not. Typical parameters that normally have to be refined are background shape, unit cell parameters, peak shape parameters, amount and for clay minerals also orientation. During the identification of the minerals, typical phases for bentonites (e.g. quartz, calcite, dolomite) can be added initially based on perhaps one strong typical reflection, while exotic phases should require much more evidence before being introduced. In this identification process different spectroscopic techniques can be very valuable as well as optical microscopy or a magnet. Identification of apatite should, if correct, be observed also in the XRF data as a corresponding amount of phosphorous. The initial manual background removal is not trivial as it is not always obvious to judge what is background or not. By judging how the software model fits with your data and what treatments that give reasonable results will be a feedback in the process. When comparing different bentonites, it is very important that this step is done in an as identical manner as possible. When all minerals have been quantified and if the chemical composition of all the included minerals is known, the chemical composition can be calculated and compared to the observed XRF data, and the montmorillonite content can be compared to the CEC of the bulk fraction divided by the CEC of the clay fraction. Example of the relative error in montmorillonite content from XRD can be expressed as a relative standard deviation (SD/measured value), and is in this case about 1 % (Table 9-1). The complementary use of X-ray diffraction (mineralogy), X-ray fluorescence (chemistry) and cation exchange capacity for characterisation is illustrated in Chapter 20 on a selection of Wyoming and Milos bentonite batches as delivered, and in the case of Wyoming also as when blended with sand.

**Table 9-1. Mineralogical composition based on XRD and standard deviation based on 3 samples taken from one small homogenized sample (MX80 1993). Mont. = montmorillonite, Ill. = illite.**

| | Mont. | Quartz | Anorthite | Cristobalite | Calcite | Albite | Pyrite | Mica/Ill. | Gypsum | Tridymite |
|---|---|---|---|---|---|---|---|---|---|---|
| **MX80 1993** | 82.83 | 3.13 | 0.57 | 1.97 | 0.17 | 3.27 | 0.13 | 5.70 | 0.87 | 1.30 |
| SD (3): | 0.83 | 0.25 | 0.60 | 0.12 | 0.12 | 0.65 | 0.06 | 0.56 | 0.06 | 0.00 |

# 10 Chemical content – X-ray fluorescence spectroscopy (XRF)

## 10.1 Introduction

The XRF method give chemical composition of the bentonite (Na and heavier elements). It is rapid, easy to evaluate and has a very high reproducibility (Table 10-1). Some grams of material are compacted to a disc at high pressure for a couple of minutes. Smaller samples can be measured as powder when placed on a mylar foil (special polyester), this will however absorb some of the low energy X-rays, and hence elements such as sodium will no longer be seen and the data also needs to be corrected by using the correct film thickness and composition.

The method is based on the commercial Omnian method, developed by the equipment supplier Panalytical. XRF data is collected under helium atmosphere at different systematic conditions controlled by a program in which different acceleration voltages and filters are used. Higher voltage gives a higher energy on input X-ray radiation and therefore excites the heavier elements. Light elements are studied at low voltage and without filters. Heavier elements are studied at high voltage and with filters to remove the information from the lighter elements. The method has been modified to measure low energy at longer time in order to improve the sensitivity to sodium which is an important component of bentonite. After modification the method takes about 20 minutes for one measurement.

Double excitation peaks may occur. This is when two photons hits the detector within a very short time course. The detected energy is then the sum of the two photons. This is something that is normally detected by the software. When using mylar film during the analysis of powder samples the mylar film impact the measurement. Contaminations in the film should be checked when changing film type and absorption by the film is calculated during the quantification of the elements. The evaluation of the standard elements of a bentonite is normally non-problematic. The equipment uses an internal calibration, but depending on the sample matrix, the method may need to be calibrated if very accurate absolute values are needed (e.g. by using dissolution and ICP-AES/MS at an external accredited laboratory). The equipment used at the laboratory can be loaded with 12 samples at the time, but if needed in the future, there are other XRF equipment with much higher X-ray intensity that can measure samples much quicker and with more efficient handling. This method is used in many mining and cement producing industries with high mass flows of natural materials. The complementary use of X-ray diffraction (mineralogy), X-ray fluorescence (chemistry) and cation exchange capacity for characterisation is illustrated in Chapter 20 on a selection of Wyoming and Milos bentonite batches as delivered, and in the case of Wyoming also as when blended with sand.

## 10.2 Analytical procedure

Bentonite powder is compacted to a disc with a diameter of about 3 cm and a thickness of at least 5 mm. If the sample amount is too small, the measurement can be done with powder. The compacted disc is placed within the sample carrousel in the XRF (a powder is placed within a sample holder with a ~4 µm mylar foil). The pre-programmed program "Omnian – Bentonite" is used, this is almost the same as the original Omnian (made by Panalytical), but the lower energies are measured for longer time. Known elements, select the "Bentonite" profile, and afterwards check the spectra to see if all details are explained. If the foil is used this should be entered into the software to improve the quantification. Example of chemical composition and standard deviation based on 21 samples taken from a small homogenized sample of MX80 from the 1993 batch can be seen in Table 10-1.

**Table 10-1. Chemical composition (wt%) and standard deviation based on 21 samples taken from a small homogenized sample of MX80 from the 1993 batch.**

| Element: | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $Fe_2O_3$ | MnO | $P_2O_5$ | $SO_3$ | Cl | $K_2O$ | CaO | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Average: | 1.694 | 2.334 | 21.325 | 67.205 | 4.930 | 0.011 | 0.010 | 0.411 | 0.010 | 0.521 | 1.386 | 0.164 |
| SD: | 0.01677 | 0.02154 | 0.02801 | 0.04197 | 0.01436 | 0.00074 | 0.00086 | 0.00499 | 0.00172 | 0.00673 | 0.01100 | 0.00145 |

# 11 Exchangeable Cations (EC)

## 11.1 Introduction

Exchangeable cations refer to the amount of each type of the exchangeable cations initially present in the interlayer space of the bentonite (Karnland 2010). These interlayer cations are charge compensating for the negative charge of the montmorillonite layers. In natural bentonite, the charge compensating cations are rarely of one element alone, but a mixture of both mono and divalent ions. The most common cations are $Na^+$, $Ca^{2+}$, $Mg^{2+}$ and $K^+$. The swelling properties are to a large extent dependent on the magnitude and the position of the layer charge, but also on the type of charge compensating cation (Karnland et al. 2006)**.**

A method for extracting exchangeable cations in bentonite was investigated and adapted for laboratory operation. The method is based on scientific article by Jackson (1975) and use ammonium ions in an alcoholic solution to exchange with $Na^+$, $Ca^{2+}$, $Mg^{2+}$ and $K^+$. Concentrations of the different extracted cations are determined by an external laboratory using inductively coupled plasma (ICP) as analysis technique. The exchange capacity of each cation is calculated and expressed in milliequivalent (meq)/100g dry weight. Total sum EC is then given by combining the calculated EC for each cation.

The unit of EC, meq/100 g, is numerically equivalent to cmol(+)/kg (the unit of CEC, see Chapter 8).

Since the bentonite (bulk material) may contain both carbonates and gypsum, the composition of the extractable exchangeable ions is determined by exchange against ammonium ions ($NH_4^+$) in an alcoholic solution in order to reduce dissolution errors (Belyayeva 1967). However, easily soluble salts, such as chlorides and carbonates of alkali metals, will still dissolve in this extractant, and the sum of the exchangeable cations often exceeds the measured CEC with the Cu-tri method of the sample (Karnland et al. 2006).

The amount of bentonite sampled for cation extraction is small (about 1 g). This makes it difficult to take a representative sample if the bulk material is not homogenous e.g. large aggregates. Therefore milled bentonite is preferred when considering sampling a homogenous bulk sample for EC determination. However it is important to verify that the milling procedure (e.g. milling time, material of the grinding jars and balls) doesn't have an unwanted effect on the bentonite and hence EC, see Section 7.2.

As the EC are reported in relation to the dry weight of a bentonite sample water content of the material also must be determined. It is essential that the weighing of bentonite for EC and water content determination is carried out at the same time and under the same conditions see Chapter 12.

## 11.2 Analytical procedure

Exchangeable cations are extracted by shaking the bentonite (1 000 g ± 10 mg) in 12.5 ml 1 M ammonium chloride solution in 80 % ethanol, on a vibrating table for approximately 30 minutes. After 5 minutes centrifugation at 2 700 RCF the supernatant is separated from the bentonite by decanting the extract to a sample tube. The extraction is repeated totally three times (i.e. same sample is extracted three times with a total volume of approx. 38 ml). After evaporation of the alcohol, the extract is filtrated (0.45 µm filter) and volume corrected with deionised water to 50 ml. The cations are analysed by inductively coupled plasma (ICP) at external laboratory. The alcohol is evaporated due to recommendations by the external laboratory for chosen analyse technique (ICPWhen evaluating the data, it is important to take into account the method uncertainties of the parameters. These uncertainties may vary depending on the laboratory method and analysis technique (e.g. ICP) for the different cations.

As the EC are reported in relation to the dry weight of a bentonite sample water content of the material also must be determined. It is essential that the weighing of bentonite for EC and water content determination is carried out at the same time and under the same conditions. The water content of a bentonite sample is determined by weighing the sample before and after oven drying at 105 °C to constant weight. The water content is reported as the mass ratio between the water and the moist material, expressed in weight percent see Chapter 12. The exchange capacity of each cation is calculated and given in meq/100g dry weight. Total sum EC is then given by combining the calculated EC for each cation (Na+, Ca2+, Mg2+ and K+), see equation 11-1 to 11-4.

Method uncertainties have not been estimated for the exchangeable cations. The method involves two steps; (1) extracting step at internal laboratory, and (2) cation analysis by ICP at external laboratory. Though the cation analyse is performed at an external laboratory it is important to take into account the method uncertainties of the parameters when sending the samples for analysis. These uncertainties may vary depending on the laboratory method and analysis technique for the different cations.

Dry sample mass ($m_{\mathrm{dry}}$) is calculated as follows:

$$m_{\mathrm{dry}} = m_{\mathrm{undried}} \times (1 - wc/100) \qquad (11\text{-}1)$$

where

| | |
|---|---|
| $m_{\mathrm{dry}}$ | dry sample mass (g) |
| $m_{\mathrm{undried}}$ | undried sample mass (g) |
| $wc$ | water content (%) |

The molar amount of each cation ($n_{\mathrm{cation}}$) is calculated as follows:

$$n_{\mathrm{cation}} = (C_{\mathrm{cation}}/M_{\mathrm{cation}}) \times V \qquad (11\text{-}2)$$

where

| | |
|---|---|
| $n_{\mathrm{cation}}$ | molar amount of each cation (mmol) |
| $C_{\mathrm{cation}}$ | measured cation concentration (mg/l) |
| $M_{\mathrm{cation}}$ | molar mass of each cation (g/mol) |
| $V$ | sample volume (liter, l) |

EC for each cation is given in meq/100 g. When"1 mmol $Na^+/K^+$ = 1 meq $Na^+/K^+$" and ½ mmol $Ca^{2+}/Mg^{2+}$ = 1 meq $Ca^{2+}/Mg^{2+}$, EC is calculated as follows:

$$EC_{\mathrm{cation}} = ((n_{\mathrm{cation}} \times ionic\ charge \times 100)/m_{\mathrm{dry}}) \qquad (11\text{-}3)$$

where

| | |
|---|---|
| $EC_{\mathrm{cation}}$ | exchange capacity of each cation (meq/100 g) |
| $n_{\mathrm{cation}}$ | molar amount of each cation (mmol) |
| $m_{\mathrm{dry}}$ | dry sample mass (g) |
| *ionic charge* | $Na^+$, $K^+$ = 1<br>$Ca^{2+}$, $Mg^{2+}$ = 2 |

Total sum EC ($EC_{\mathrm{sum}}$) for cations $Na^+$, $Ca^{2+}$, $Mg^{2+}$ and $K^+$ is calculated as follows:

$$EC_{\mathrm{sum}} = EC_{\mathrm{Na}} + EC_{\mathrm{Ca}} + EC_{\mathrm{Mg}} + EC_{\mathrm{K}} \qquad (11\text{-}4)$$

where

| | |
|---|---|
| $EC_{\mathrm{sum}}$ | Total summa-EC (meq/100g) |
| $EC_{\mathrm{cation}}$ | Exchange capacity of each cation (meq/100 g) |

# 12 Water content

## 12.1 Introduction

Water in the bentonite is in the mineral montmorillonite, a layered silicate with hydrated interlayer ions. These ions are usually $Na^+$, $Ca^{2+}$, $Mg^{2+}$ or $K^+$ see Chapter 11. Depending on the type of interlayer ions and ambient relative humidity, the bentonite will have more or less water in the structure in equilibrium with the environment. When the clay water varies with the particular ambient relative humidity, it is often important to relate the properties of the clay to its dry weight. After drying at 300 °C for 2 hours, the last water existing between the layers disappears (Brindley and Brown 1980).

Additional water is lost from the clay at higher temperatures (about 450–750 °C), but this water is not from hydrated interlayer ions. The water lost at these high temperatures is from dehydroxylation reactions of montmorillonite crystal structure (Newman 1987). It is important that the determination of water content is always done the same way, in order to obtain comparable results. Analysis where water content plays an important role is the cation exchange capacity (CEC, see Chapter 8) and the type of exchangeable cations (EC, see Chapter 11).

Geotechnical standard for soil, SIS-CEN ISO/TS 17892-1:2005 was investigated and adapted for laboratory operation of bentonite. The practical procedure for determining the water content of the bentonite is to dry the bentonite in a ventilated oven at a temperature of 105 °C ± 5 °C for at least 24 hours. The mass loss of water is determined by a laboratory balance. The mass ratio between the water and the dry material is refered to as geotechnical water content (*w*), while the mass ratio between the water and the moist material is refered to as general water content (*wc*). Both (*w*) and (*wc*) are expressed in weight percent.

How the bentonite should be stored prior to analysis depends on the purpose of the water content determination, see Section 12.2. If the material is kept incorrectly, for example, with free access to moisture, the water content would change compared to how it looked at the time of sample extraction.

According to the geotechnical standard the minimum sample mass should not be less than 25 g (grain size diameter < 1.0 mm). In some cases this amount of sample is not available and only a smaller sample mass can be sampled. Using a test specimen smaller than the minimum mass indicated requires discretion, though it may be adequate for the purpose of the test. If the sample amount is limited, this method recommends a minimum sample mass of 2 g of moisture determination. If the sample is compact or if there are larger pieces (sets), these should first be broken, crushed or milled. However it is important to verify that the milling procedure (e.g. milling time, material of the grinding jars and balls) doesn't have an unwanted effect on the bentonite, see Section 7.2.

Since dry bentonite can absorb moisture, dried samples should be removed prior to placing undried bentonite in the oven. This requirement is not applicable if the previously dried samples will remain in the drying oven for a further period of approximately 16 hours. Method uncertainty has not been estimated for determination of water content.

## 12.2 Analytical procedure

If the purpose is to determine the water content of the bentonite material at the time of the sampling, the bentonite is packaged in air-tight and corrosion resistant sampling vessel immediately after sample extraction. Storage of these sampling vessels shall take place at 3–30 °C and kept away from direct sunlight. The water content should be determined as soon as practicable after sampling, but no later than 24 hours if the bentonite is stored in cans with tight-fitting lids. If the purpose is to determine the water content of the bentonite for the correction of the CEC and EC, it is rather important that the water content determination is performed at exactly the same time and under the same conditions as the weigh-in for the CEC and EC. This is because the CEC and EC for bentonite clay are given in relation to the dry weight at the prevailing conditions, see Chapter 8 and 11.

Suitable corrosion resistant sample containers, such as aluminium tins, are used for sample weighing and determination of water content. The drying oven shall preferably be of the forced-draft type, and capable of maintaining a uniform temperature of 105 °C ± 5 °C throughout the drying chamber. For ovens of the forced-draft type, the air circulation may not be so strong that any transport of particles can take place.

The bentonite sample is placed in a clean empty aluminium tin of known mass. Using a laboratory balance the mass of the aluminium tin and the bentonite sample is determined. Note the values of the different weights. The samples are dried in a drying oven at 105 °C ± 5 °C for 24 hours. After at least 24 hours drying the total weight of the aluminium tin and the dried sample is weighed. The balance shall have a minimum resolution of 0.001g. Using a sample specimen smaller than 25 g requires discretion se Section 12.1. The general water content (*wc*) of the bentonite sample are calculated as follows:

$$wc = \frac{m_1 - m_2}{m_1 - m_c}\, x\, 100 = \frac{m_w}{m_{tot}}\, x\, 100 \tag{12-1}$$

where

| | |
|---|---|
| $wc$ | water content (general) (%) |
| $m_1$ | mass of sample container + undried sample (g) |
| $m_2$ | mass of sample container + dried sample (g) |
| $m_c$ | mass of sample container (g) |
| $m_w$ | mass of pore water (g) |
| $m_{tot}$ | total mass of pore water + grains (g) |

The geotechnical water content can also be expressed as; water content (*wc*) = mass of pore water ($m_w$)/total mass ($m_{tot}$).

The water content (*w*) of the bentonite sample is calculated as follows:

$$w = \frac{m_1 - m_2}{m_2 - m_c}\, x\, 100 = \frac{m_w}{m_s}\, x\, 100 \tag{12-2}$$

where

| | |
|---|---|
| $w$ | water content (geotechnical) (%) |
| $m_1$ | mass of sample container + undried sample (g) |
| $m_2$ | mass of sample container + dried sample (g) |
| $m_c$ | mass of sample container (g) |
| $m_w$ | mass of pore water (g) |
| $m_s$ | mass of grains (g) |

The water content can also be expressed as; water content (*w*) = mass of pore water ($m_w$)/mass of grains ($m_s$).

# 13 Bulk density

## 13.1 Introduction

The bentonite buffer and backfill components in the repository are all in the compacted state. Many of the bentonite properties are functions of or have empirical correlations to the compaction density. Higher densities generally give for a specific bentonite: higher swelling pressure, lower plasticity and lower hydraulic conductivity. Density is denominated mainly in two ways: (1) the bulk density (the total density) and (2) the dry density (theoretical density after subtraction of the water content). A bentonite block with a bulk density of 1 500 kg/m$^3$ that has a water content of 33.3 % has 1 500 × 0.333 = 500 kg of water included, hence the dry density of the block is only 1 000 kg/m$^3$.

The method used for determination of bulk density of bentonite is based on geotechnical standard for soil, SIS-CEN ISO/TS 17892-1:2005. The test procedure is based on the standard method "immersion in fluid" and includes the determination of bulk density and dry density of a specimen of natural or compacted bentonite by measuring its mass in air and its apparent mass when suspended in fluid. The method may be used when lumps of material of suitable size can be obtained. Since bentonite and water may lead to dissolution of some minerals paraffin oil is used instead of water as the liquid. When calculating the bulk- and dry density, the paraffin oil density is taken into account. Instead of using a cradle when immersing the bentonite in paraffin oil a metal wire or thread is tied around the sample. The bulk density is determined by hanging the sample in the metal wire or thread under a balance. The sample is then weighed, first in air and then submerged into paraffin oil. The sample volume is then calculated, see Section 13.2. For calculation of the dry density, water content also is used, see Chapter 12.

If the material is kept incorrectly, for example, with free access to moisture, the water content would change compared to how it looked at the time of sample uplift andthereby impact the calculated dry density of the sample.

## 13.2 Analytical procedure

If the purpose is to determine the density of the bentonite material at the time of the sampling, the bentonite is packaged in air-tight and corrosion resistant sampling vessel immediately after sample uplift. Storage of these sampling vessels shall take place at 3–30 °C and kept away from direct sunlight. The density should be determined as soon as practicable after sampling (e.g. after sawing of bentonite profile from field experiment), but no longer than 24 hours if the bentonite is stored in cans with tight-fitting lids. Samples of approximately 10 cm$^3$ are used.

### *Determination of paraffin oil density*

Paraffin oil density is always determined when a new batch is put into use. The paraffin oil density is determined in the following steps:

1) Weigh an empty 2 000 ml volumetric flask and note the mass ($m_{\text{flask}}$).
2) Fill the volumetric flask to the mark with water with known temperature. Note the temperature of the water and the mass of the volumetric flask filled with water ($m_{\text{water+flask}}$).
3) Empty the volumetric flask and let dry. Then fill the volumetric flask with paraffin oil to the mark and let stand for about 15 minutes or until no air bubbles are seen. Note the mass of the volumetric flask and the paraffin oil ($m_{\text{oil+flask}}$).

Sample volume ($V_{\text{sample}}$) is calculated as follows:

$$V_{\text{sample}} = (m_{\text{water+flask}} - m_{\text{flask}})/\rho_{\text{water}} \qquad (13\text{-}1)$$

where

| | |
|---|---|
| $V_{\mathrm{sample}}$ | sample volume (cm$^3$) |
| $m_{\mathrm{water+flask}}$ | mass of volumetric flask + water (g) |
| $m_{\mathrm{flask}}$ | mass of volumetric flask (g) |
| $\rho_{\mathrm{water}}$ | table value for density of water at a certain temperature (g/cm$^3$) |

Paraffin oil density ($\rho_{\mathrm{oil}}$) is calculated as follows:

$$\rho_{\mathrm{oil}} = (m_{\mathrm{oil+flask}} - m_{\mathrm{flask}})/V_{\mathrm{sample}} \tag{13-2}$$

where

| | |
|---|---|
| $\rho_{\mathrm{oil}}$ | paraffin oil density (g/cm$^3$) |
| $m_{\mathrm{oil+flask}}$ | mass of volumetric flask and paraffin oil (g) |
| $m_{\mathrm{flask}}$ | mass of volumetric flask (g) |
| $V_{\mathrm{sample}}$ | sample volume (cm$^3$) |

### *Determination of bulk density of the bentonite*

Bulk density of the bentonite is determined in the following steps:

1) Weigh a metal wire or thread and note the mass ($m_{\mathrm{thread}}$).
2) Spin one end of the wire or thread around the bentonite sample. Make a loop at the other end of the wire and hang the sample under the balance. Note the mass of the bentonite sample and the thread in air ($m_{\mathrm{sample+thread}}$).
3) Lower the bentonite sample in the container with density determined paraffin oil. The container shall be filled with paraffin oil almost to the top. Ensure that the sample is properly immersed and not in contact with the bottom, surface or sides of the container. Note the mass immediately when immersed ($m_{\mathrm{sample+thread}}$) so that the oil does not have time to be absorbed by the clay. Ensure that no air bubbles are trapped under the test specimen.

The dry density of the bentonite can be calculated from the sample's water content (amount of water related to the wet weight of sample) alternatively by the sample's water content (amount of water in relation to dry weight of sample). Calculation of water content of a bentonite sample is described in Section 12.2.

Bentonite sample mass ($m_{\mathrm{sample}}$) in air or in oil is calculated as follows:

$$m_{\mathrm{sample}} = m_{\mathrm{sample+thread}} - m_{\mathrm{thread}} \tag{13-3}$$

where

| | |
|---|---|
| $m_{\mathrm{sample}}$ | sample mass in air ($m_{\mathrm{air}}$) or in paraffin oil ($m_{\mathrm{oil}}$) (g) |
| $m_{\mathrm{sample+thread}}$ | mass of the sample + thread (g) |
| $m_{\mathrm{thread}}$ | mass of the thread (g) |

Sample volume ($V_{\mathrm{sample}}$) is calculated as follows:

$$V_{\mathrm{sample}} = (m_{\mathrm{air}} - m_{\mathrm{oil}})/\rho_{\mathrm{oil}} \tag{13-4}$$

where

| | |
|---|---|
| $V_{\mathrm{sample}}$ | sample volume (cm$^3$) |
| $m_{\mathrm{air}}$ | sample mass in air (g) |
| $m_{\mathrm{oil}}$ | sample mass in paraffin oil (g) |
| $\rho_{\mathrm{oil}}$ | paraffin oil density (g/cm$^3$) |

Bulk density ($\rho$) of bentonite is calculated as follows:

$$\rho = m_{\text{sample}}/V_{\text{sample}} \tag{13-5}$$

where

| | |
|---|---|
| $\rho$ | bulk density (g/cm$^3$) |
| $m_{\text{sample}}$ | sample mass (g) |
| $V_{\text{sample}}$ | sample volume (cm$^3$) |

Dry density ($\rho_d$) of the bentonite, calculated from the water content of the sample:

$$\rho_d = \rho \times (100-wc/100) \tag{13-6}$$

where

| | |
|---|---|
| $\rho_d$ | dry density (g/cm$^3$) |
| $\rho$ | bulk density (g/cm$^3$) |
| $wc$ | water content (%) |

Dry density ($\rho_d$) of the bentonite, calculated from the water content of the sample:

$$\rho_d = \rho/(1+w) \tag{13-7}$$

where

| | |
|---|---|
| $\rho_d$ | dry density (g/cm$^3$) |
| $\rho$ | bulk density (g/cm$^3$) |
| $w$ | water content expressed as decimal fraction of the dry mass |

# 14 Granule size distribution

## 14.1 Introduction

Granule size distribution of the bentonite is an important parameter when compacting bentonite blocks. Studies have shown that this parameter mainly affects the strength of the blocks, stability on corners and edges, and cracking (Sandén et al. 2015). If the bentonite only contains fine material the venting during the compaction is reduced, e.g. closing some air into block which that may later cause cracks. A too fine material makes the material handling difficult because it forms a lot of dust. If bentonite instead only contains coarse material there may be problems with the block quality in terms of corners and block sites that become brittle and material can easily fall off. Another problem is that the optimum granular size distribution to manufacture blocks seem to vary between different bentonites which means that tests will be necessary when the material is changed.

Granule distribution is often confused with the grain size distribution which is something completely different. With granule we mean the conglomerate, which is made up of small grains and that can only hold together under dry conditions. To determine the grain size distribution includes dispersing the material in water to dissolve all grains that have formed these granules/lumps. For many soils it is not much difference if water is used or not, but for bentonite clay the result becomes completely different because the granules are dissolved in water and you get many very fine particles.

Determination of grain size distribution of a soil material is described in the SIS-CEN ISO/TS 17892-4:2013. This description, however, also comprises wet screening and hydrometer analysis, which means that the method as a whole cannot be used in determining granular size distribution of a bentonite clay. However, some parts describing the procedure when dry sieving of material can be used.

### *Interferences and sources of error*

An obvious source of error is the difficulty in taking a representative sample from e.g. a large bag (big bag). In some materials, there may be a separation during transport, which means that the top layer of the bag is not representative of the whole bag.

## 14.2 Analytical procedure

1. Take a sample of about 5 kg (not from the surface in the big bags, dig a couple of inches down).

2. This sample is then poured into a so-called dividing apparatus and broken until the test sample is about 500 grams.

3 The following mesh sizes are recommended for sieving (Sandén et al. 2014): 16, 8, 5.6, 4, 2, 1, 0.5, 0.25; 0.125 and 0.075 mm

To prevent damage to the granules use manual sieving only (not with a machine).

The procedure for manual sieving is as follows:

1. All sievs are inspected and cleaned of any materials from previous use.

2. All sievs are weighed individually.

3. Place the sievs on top of each other in the right order, the largest mesh top and bottom, and at least one bottom part which collects the material that might fall through the sieve with a minimum mesh size.

4. The sample is poured into the top sieve.

5. Shake the entire stack of sieves manually. Gradually, you can loosen and remove the top sieves when all material smaller than the current mesh is judged to have fallen down.

6. When it is judged that all the material that remains on a screen is larger than the current mesh, it is weighed with the remaining material. This work is continued until all sieves and the bottom part has been considered.

The mass of bentonite found at each size gives the granular size distribution.

# 15 Swelling pressure and hydraulic conductivity

## 15.1 Introduction

The main properties of the buffer and the backfill in the KBS3-concept, see Chapter 1, are depending on both the swelling pressure ($P_s$) and the hydraulic conductivity ($k_w$) of the materials which the buffer and backfill are made of. The buffer shall be designed such as the swelling pressure should be between 3–10 MPa and the hydraulic conductivity should not be higher than 1E-12 m/s. The swelling pressure for the backfill should not be lower than 1 MPa and the hydraulic conductivity should not be higher than 1E-10 m/s.

The method for determining the swelling pressure and the hydraulic conductivity are intimately combined in a sequence of steps.

The overall procedure is very briefly: (1) compaction of bentonite to correct density (in the test cell or outside in a mold), (2) saturation with deionised water of the bentonite in the test cell (Figure 15-1) until the swelling pressure is stabilised, (3) the cell is pressurised with water and the flow rate through the sample give the hydraulic conductivity, (4) the external solution is changed from water to 1 M $CaCl_2$ solution (Figure 15-2), the swelling pressure is documented when stabilised, and (5) hydraulic conductivity is performed with the salt solution.

### *Swelling pressure*

If a bentonite swells and completely fill a given volume, and further swelling is thereby prevented although it has access to water, a pressure to equalize the water chemical potential is developed. The term swelling pressure for a bentonite is thus defined as the pressure developed in a limited volume of bentonite which is in equilibrium with an external water solution. The definition is not obvious since the pressure can be developed because of swelling even when equilibrium has not been reached.

A condition for the equilibrium is that water can move freely between the bentonite and the external water solution, while the bentonite cannot move out into the external water solution. Both in a real repository and in laboratory tests, any ions that are not counter ions (i.e. not part of the montmorillonite) will at equilibrium be distributed differently between the water in the bentonite and the external water solution. These ions thus affect the water chemical potential both in the water solution and in the bentonite, but in different ways. Generally, a measured swelling pressure depends on the conditions both inside the bentonite and in the aqueous solution.

At least the following variables of the bentonite are expected to affect the swelling pressure:

1. Compaction dry density (Karnland 2010).
2. Montmorillonite content (Karnland 2010).
3. Montmorillonite type of counter ions (e.g. Norrish 1954, Segad et al. 2010).
4. Concentration of ions in the external solution (e.g. Karnland et al. 2005, Svensson and Hansen 2013).
5. Temperature (e.g. Birgersson et al. 2008, Svensson and Hansen 2010).
6. Hysteresis effects. The measured swelling pressure is depending on how the specimen has reached equilibrium e.g. during swelling or compression (Börgesson et al. 1988).
7. Montmorillonite layer charge is expected to have an impact (e.g. Laird 2006).
8. Montmorillonite particle size may have an impact (Segad et al. 2012).
9. External water pressure.

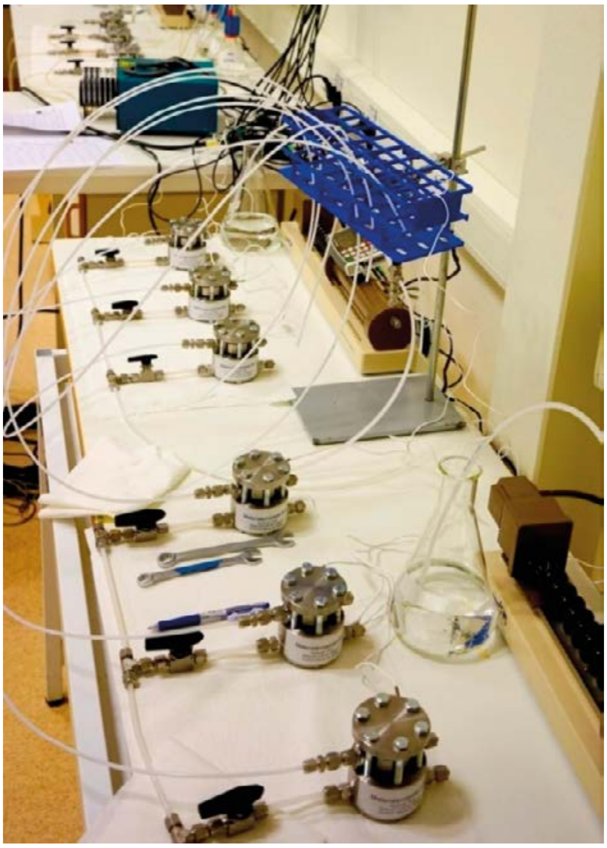

***Figure 15-1.** The test cells for swelling pressure and hydraulic conductivity measurements.*

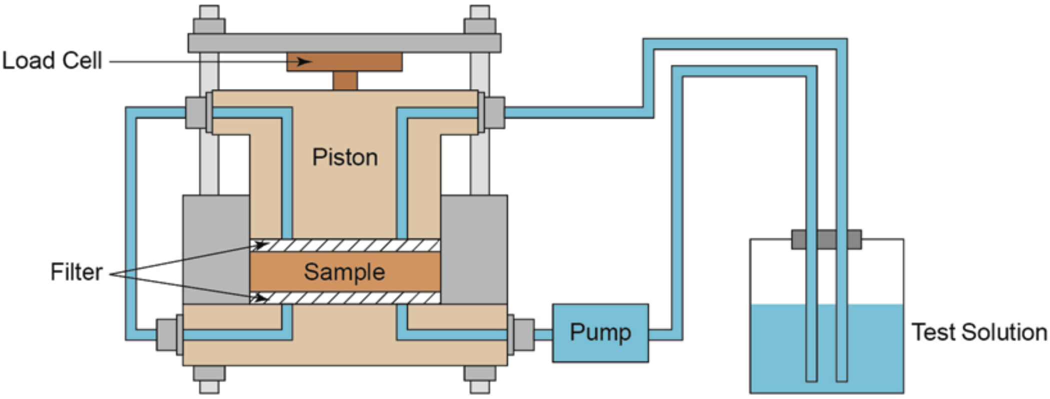

***Figure 15-2.** Schematic drawing of a test cell for determining the swelling pressure and hydraulic conductivity.*

### Hydraulic conductivity

If the bentonite has access to two water solutions with different chemical potential, the equilibrium may not be reached until the chemical potential is equalized for the external solutions, which spontaneously occurs by transportation of water from the solution with a higher potential to the one with lower potential. If the potential difference is maintained, a steady state will be reached, resulting in a constant mass transport of water through the bentonite. The mass transport trough the bentonite is approximately linearly dependent on the difference in chemical potential, which allows the evaluation if the water transport can be made according to Darcy's law, see Section 15.2, and thus the result can be expressed as hydraulic conductivity. In experiment performed in the laboratory, it is usually advantageous to maintain a difference in chemical potential by applying a pressure differential between the aqueous solutions with pressure devices which can be set to a specific value with high accuracy.

## 15.2 Analytical procedure

The measurements of swelling pressure and hydraulic conductivity for a bentonite are carried out with deionised water and with a 1 M $CaCl_2$ solution.

When the sample is in contact with deionised water, a transient state will be present, but the measurements are still expected to provide approximate information about the likely maximum pressure for the bentonite at conditions expected in a repository.

When the sample is in contact with the calcium chloride solution the counter ions in the bentonite will be changed to only calcium, and the results thus provide information on the swelling pressure and hydraulic conductivity at extremely unfavorable conditions both concerning the type and the amount of counter ions not belonging to the montmorillonite.

The method for determining the swelling pressure and hydraulic conductivity has been developed over a 20-year period primarily by personnel at the company Clay Technology AB in Lund. The method is described in detail in Karnland et al. (2006).

To determine the swelling pressure and hydraulic conductivity at a predetermined density is normally difficult to implement with good precision. The preparation of the sample is therefore based on a desired density of the samples. After the measurements of the swelling pressure and hydraulic conductivity are performed, determinations of the density and water content on the specimen are made. It is these determinations, together with measurements of the swelling pressure and hydraulic conductivity, which represents the results from the tests.

The swelling pressure and the hydraulic conductivity for a specific bentonite is a function of the density but also depending on the conditions under which water saturation of the samples has been made. A sample which is allowed to swell during water saturation has different swelling pressure and hydraulic conductivity compared to a sample which has been compressed or held at constant volume. The chosen preparation process strives to get a sample with constant volume during the saturation phase. This may in some cases be difficult to achieve, especially for samples with high density.

The prepared samples for the tests are small in order to ensure that the exchange of ion in the material can be done in a reasonable time. This may imply that it can be difficult to take a representative sample of the bentonite, especially if it is not homogeneous but contain large aggregates.

The small sample may also affect the evaluation of the hydraulic conductivity since it might be difficult to ensure that the right pore pressure gradient is applied over the sample. This is more obvious for samples with low densities where the risk is higher that the filter might be clogged with bentonite or salt.

Furthermore, the small samples may also affect the precision in the determination of the density and water content.

### *Testing procedure*

The tests are performed according to the following (Karnland et al. 2006):

- The selected homogenous material is packed into the swelling pressure cell to a predetermined dry density. The specimen has a diameter of 35 mm and an approximate height of 5 mm.
- The specimen is saturated with deionised water and the swelling pressure measured with an external load cell is recorded continuously (P), see Figure 15-2. This is done over a time period of about one week. The swelling pressure is determined as the recorded load divided with the cross sectional area of the specimen (A).
- The hydraulic conductivity of the specimen is first determined with deionised water. The determination is made by applying a constant pore pressure gradient over the specimen while the amount of water per time unit (q) is measured continuously. The gradient (i) is defined as the applied pressure in meters of water column divided by the height of the sample. The evaluation is made according to Darcy's law, where the hydraulic conductivity ($k_w$) is determined as $k_w = q/(A \times i)$ where A is the cross sectional area of the specimen. The measurement of the hydraulic conductivity continues for about one week.

- A 1 M $CaCl_2$ solution is pumped through the filters at the same pressure on both sides of the specimen during continuous measurement of the swelling pressure. The contact with the calcium chloride solution changes the counter-ions in the bentonite to calcium alone, and the results thus provide information on the swelling pressure and hydraulic conductivity at extremely unfavourable conditions both with respect to the type of counter-ion and high ionic strength. The process where the counter ions are changed to calcium in the specimen takes about 1 week.
- The hydraulic conductivity of the sample is determined with the calcium chloride solution for about one week.
- The specimen is taken out of the swelling pressure cell, and its bulk density (ρ) and water content (w) is determined. The bulk density is determined by weighting a sample both in air and submerged in paraffin oil with known density. The water content is determined by drying a sample in an oven at a temperature of 105 C° for 24 hours. With the known density and water content the dry density ($\rho_d$) can be calculated:

$$\rho_d = \frac{\rho}{1 + w}$$

### Calibration

The calibration of the load cell used for determining the swelling pressure, see Figure 15-2, is made prior to the starting of the experiments. This is made with a reference load cell which is checked regularly. The load cell is also checked after the test has been finalised, also with the reference load cell.

The equipment used for applying the constant pore pressure gradient (e.g. a GDS device) is also checked on a regular basis. This is done by using a pressure gauge that is controlled.

### Analysis of data

The results from the measuring of the hydraulic conductivity and swelling pressure of a bentonite are reported together with base data such as water content, bulk density and dry density of the investigated specimens. It is also important to report the pore pressure gradient used at the measuring of the hydraulic conductivity of the bentonite. In Table 15-1 and Table 15-2, data from investigation of two bentonites, MX-80 and ASHA are presented.

### Estimation of errors at the determination of swelling pressure and hydraulic conductivity of bentonite

The relationship between the dry density and the swelling pressure of a bentonite is typically exponential (Karnland et al. 2006). This is exemplified in Figure 15-3, where the determinations made on the MX-80 is plotted as a function of the dry density of the specimen. One way to get an estimation of the errors witch are related to the measurements is to evaluate the mean and standard deviation of the swelling pressure measurements after the trend values are subtracted from values. The so-called residuals are evaluated. The residuals for the swelling pressure measurements are presented in Figure 15-4. Analysis of the residuals show that determinations made with deionized water has a mean of about 0 kPa, and a standard deviation of 620 kPa. The corresponding values for the determinations made at 1 M CalCl2 is 4 kPa and 673 kPa

Corresponding analyses on the hydraulic conductivity is more difficult to do, since the the hydraulic conductivity plotted as a function of dry density normally follows a straight line in a lin-log diagram, see Figure 15-5 This implies that a small variation of the dry density results in a large change of the hydraulic conductivity.

**Table 15-1. Evaluated swelling pressure and hydraulic conductivity on MX-80.**

| Test no | Deionised water | | | 1 M $CaCl_2$-solution | | | Bulk-density, $\rho$ ($kg/m^3$) | Water-cont., w (%) | Dry-density, $\rho_d$ ($kg/m^3$) |
|---|---|---|---|---|---|---|---|---|---|
| | Swelling pr (kPa) | Gradient (–) | Hydr. cond (m/s) | Swelling pr (kPa) | Gradient (–) | Hydr. cond (m/s) | | | |
| 1 | 3 299 | 20 803 | 1.29E–13 | 1 807 | 16 643 | 1.72E–13 | 1 904 | 34.5 | 1 416 |
| 2 | 6 989 | 21 237 | 6.34E–14 | 5 448 | 16 989 | 4.77E–14 | 1 988 | 29.4 | 1 536 |
| 3 | 8 028 | 20 698 | 5.49E–14 | 6 318 | 16 558 | 4.03E–14 | 1 992 | 28.5 | 1 551 |
| 4 | 5 078 | 16 310 | 4.65E–14 | 4 095 | 16 310 | 7.44E–14 | 1 977 | 32.8 | 1 489 |
| 5 | 5 237 | 16 148 | 8.29E–14 | 3 261 | 16 148 | 6.12E–14 | 1 947 | 30.9 | 1 487 |
| 6 | 5 668 | 16 069 | 6.98E–14 | 3 586 | 16 069 | 9.40E–14 | 1 948 | 30.3 | 1 495 |
| 7 | 6 479 | 16 269 | 4.62E–14 | 4 519 | 16 269 | 5.81E–14 | 1 981 | 30.2 | 1 522 |
| 8 | 6 639 | 16 172 | 6.05E–14 | 4 732 | 16 172 | 4.01E–14 | 1 991 | 29.5 | 1 538 |
| 9 | 6 258 | 15 974 | 3.94E–14 | 4 206 | 15 974 | 6.58E–14 | 1 982 | 30.1 | 1 524 |
| 10 | 7 398 | 16 884 | 4.99E–14 | 5 473 | 16 884 | 3.69E–14 | 2 012 | 28.0 | 1 572 |
| 11 | 7 808 | 16 508 | 5.54E–14 | 5 653 | 16 508 | 4.40E–14 | 1 977 | 27.6 | 1 550 |
| 12 | 7 849 | 16 668 | 5.53E–14 | 5 657 | 16 668 | 4.39E–14 | 2 001 | 28.0 | 1 563 |
| 13 | 1 721 | 11 141 | 2.26E–13 | 730 | 5 570 | 3.78E–13 | 1 879 | 38.2 | 1 359 |
| 14 | 2 078 | 11 045 | 1.70E–13 | 954 | 5 523 | 2.56E–13 | 1 869 | 35.6 | 1 378 |
| 15 | 4 818 | 10 971 | 1.02E–13 | 2 739 | 6 116 | 5.40E–14 | 1 937 | 29.1 | 1 500 |
| 16 | 4 840 | 20 347 | 7.10E–14 | 2 945 | 20 347 | 8.99E–14 | 1 958 | 32.7 | 1 476 |
| 17 | 10 619 | 20 226 | 5.53E–14 | 8 869 | 20 226 | 4.73E–14 | 1 990 | 25.0 | 1 591 |
| 18 | 12 924 | 20 510 | 4.30E–14 | 11 684 | 20 510 | 3.82E–14 | 2 011 | 23.4 | 1 630 |
| 19 | 6 716 | 43 750 | 6.54E–14 | 4 664 | 32 812 | 5.76E–14 | 1 980 | 28.2 | 1 545 |
| 20 | 11 017 | 38 889 | 2.47E–14 | 9 500 | 29 166 | 2.82E–14 | 2 036 | 25.4 | 1 624 |
| 21 | 18 005 | 40 451 | 1.41E–14 | 17 508 | 30 338 | 1.59E–14 | 2 068 | 24.1 | 1 667 |

**Table 15-2. Evaluated swelling pressure and hydraulic conductivity on ASHA.**

| Test no | Deionised water | | | 1 M $CaCl_2$-solution | | | Bulk-density, $\rho$ ($kg/m^3$) | Water-cont., w (%) | Dry-density, $\rho_d$ ($kg/m^3$) |
|---|---|---|---|---|---|---|---|---|---|
| | Swelling pr (kPa) | Gradient (–) | Hydr. cond (m/s) | Swelling pr (kPa) | Gradient (–) | Hydr. cond (m/s) | | | |
| 1 | 851 | 7 551 | 2.35E–12 | 570 | 4 719 | 3.37E–12 | 1 829 | 50.1 | 1 219 |
| 2 | 2 249 | 7 414 | 8.11E–13 | 1 443 | 7 414 | 8.64E–13 | 1 879 | 38.2 | 1 359 |
| 3 | 4 612 | 7 414 | 3.55E–13 | 3 590 | 7 414 | 3.14E–13 | 1 952 | 32.7 | 1 471 |
| 4 | 1 180 | 11 080 | 1.12E–12 | 938 | 8 864 | 1.28E–12 | 1 867 | 43.8 | 1 299 |
| 5 | 1 984 | 10 349 | 1.22E–12 | 1 344 | 8 279 | 1.24E–12 | 1 928 | 44.8 | 1 331 |
| 6 | 2 493 | 9 994 | 6.71E–13 | 1 765 | 7 995 | 7.30E–13 | 1 910 | 37.3 | 1 391 |
| 7 | 873 | 2 080 | 3.40E–12 | 524 | 2 080 | 4.55E–12 | 1 739 | 42.6 | 1 220 |
| 8 | 1 337 | 1 970 | 1.57E–12 | 855 | 1 970 | 1.83E–12 | 1 858 | 45.0 | 1 281 |
| 9 | 3 228 | 2 080 | 5.37E–13 | 2 356 | 2 080 | 6.89E–13 | 1 890 | 34.1 | 1 409 |
| 10 | 743 | 2 929 | 1.93E–12 | 379 | 2 929 | 2.16E–12 | 1 828 | 44.4 | 1 266 |
| 11 | 1 224 | 2 989 | 1.04E–12 | 675 | 2 989 | 1.72E–12 | 1 841 | 41.4 | 1 303 |
| 12 | 3 652 | 6 092 | 3.23E–13 | 2 551 | 3 046 | 4.02E–13 | 1 949 | 35.2 | 1 442 |
| 13 | 1 681 | 6 104 | 1.65E–12 | 1 056 | 6 104 | 1.97E–12 | 1 866 | 39.9 | 1 333 |
| 14 | 1 366 | 5 661 | 1.15E–12 | 781 | 5 661 | 1.29E–12 | 1 851 | 39.2 | 1 330 |
| 15 | 3 703 | 5 909 | 4.09E–13 | 2 582 | 5 909 | 3.78E–13 | 1 933 | 33.2 | 1 451 |
| 16 | 4 286 | 15 307 | 3.50E–13 | 3 277 | 15 307 | 3.77E–13 | 1 920 | 34.6 | 1 426 |
| 17 | 9 665 | 16 014 | 1.75E–13 | 8 976 | 16 014 | 1.64E–13 | 2 016 | 30.3 | 1 548 |
| 18 | 13 349 | 15 467 | 1.26E–13 | 13 103 | 15 467 | 1.15E–13 | 2 041 | 27.8 | 1 596 |

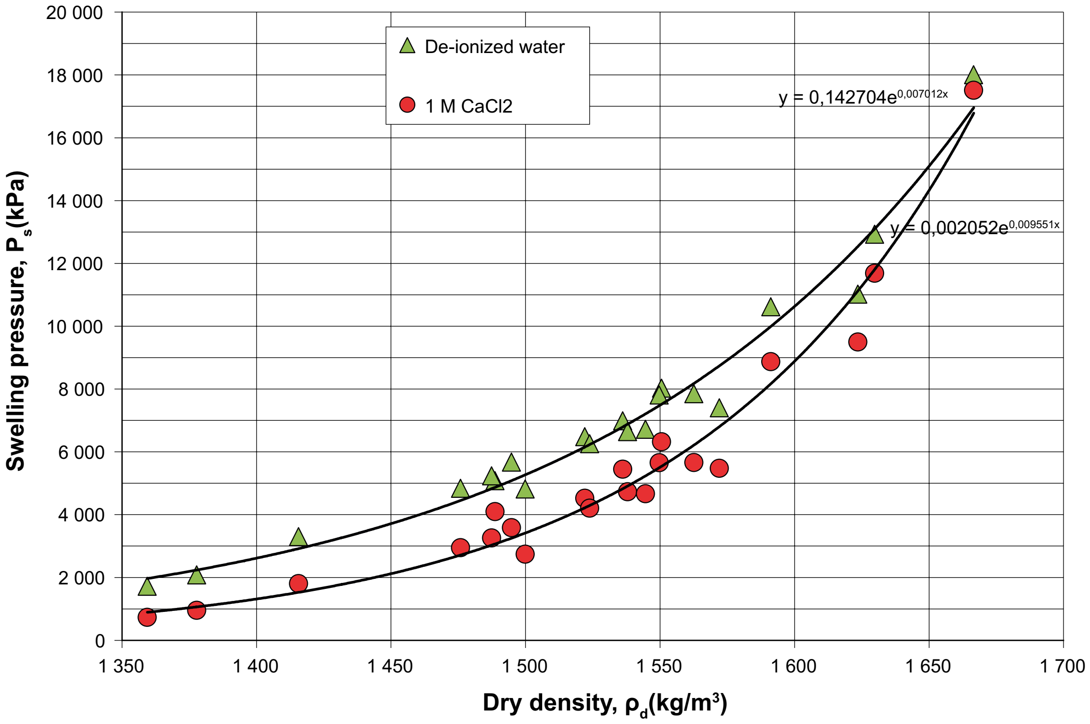

*Figure 15-3. Measured swelling pressure as a function of the dry density of the bentonite MX-80. The best fitting exponential equations are also given.*

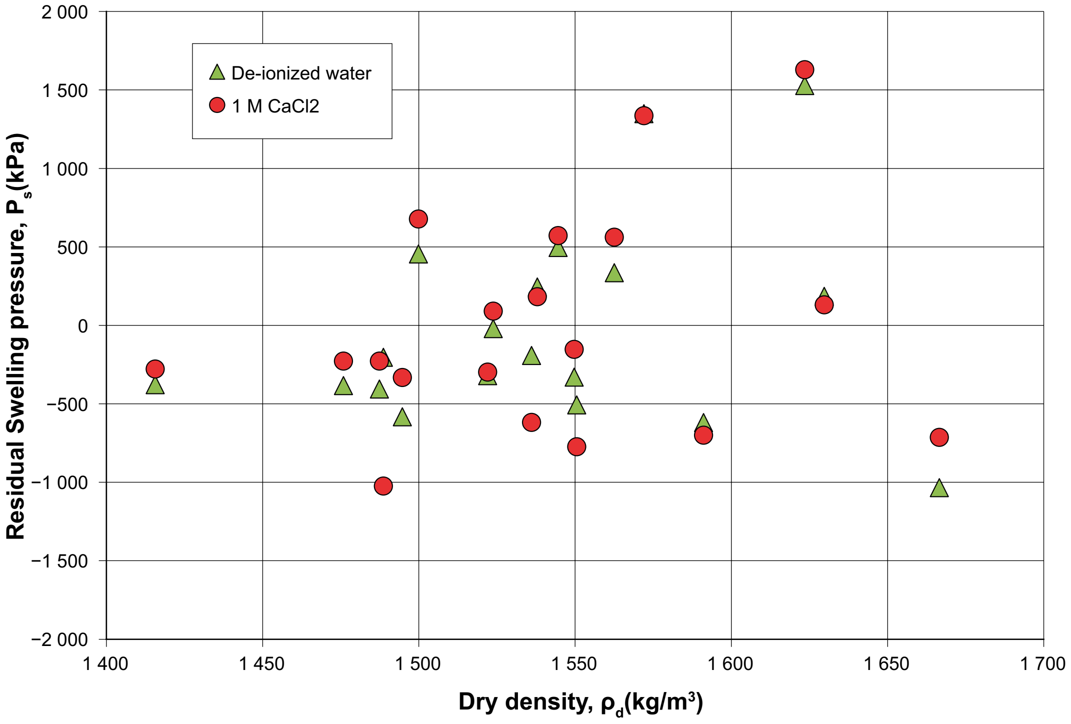

*Figure 15-4. The residuals of the swelling pressure as function of the dry density evaluated from measurements made on MX-80.*

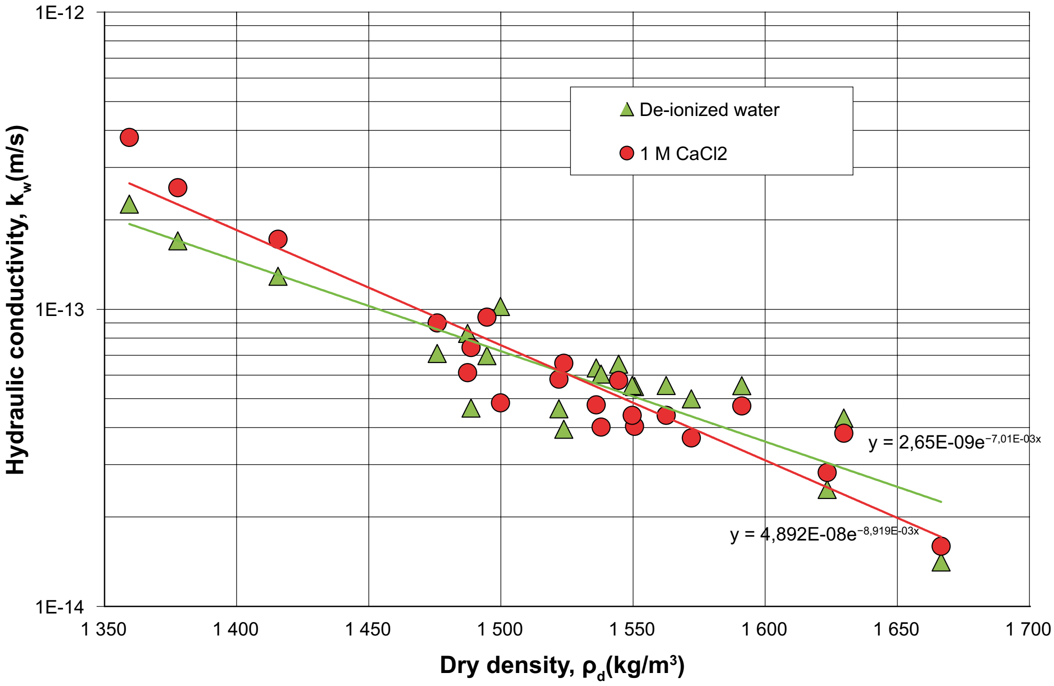

***Figure 15-5.*** *Measured hydraulic conductivity as a function of the dry density of the bentonite MX-80.*

# 16 Shear strength

The buffer around the canister will, besides minimising the risk for radio nuclides to be spread, also function as mechanical protection of the canister. Rock shear movements may occur when the stresses in bedrock are released. Depending on the mechanical properties of the buffer, the rock shear movements may cause the insert in the canister to collapse or deform to such extent that the deformation of the copper shell will result in a breach and loss of the containment. The higher the shear strength of the buffer is the higher the stresses in the canister will be.

The buffer shall be designed such that the largest shear movement expected to occur in the deposition hole, i.e. a 5 cm displacement at the rate of 1 m/s, will not cause excessive shear strain on canister. This implies that the buffer must not be too stiff.

Modelling and laboratory test have shown that the stresses on the canister will be reduced to acceptable level if the shear strength of the buffer, measured with a so called unconfined compression test at deformation rate of 0.8 % minimum, is limited to a maximum value of 4000 kPa, see also Section 4.1.

## 16.1 Test method

The shear strength can be determined by the unconfined compression test. In this kind of test a sample is compressed axially with a constant rate of strain with no radial confinement or external radial stress. The test can be regarded as a consolidated unconfined compression test, since the fully water saturated samples are attained by a negative pore pressure, which is similar to the swelling pressure.

The specimens used for the test are relatively small. The dimeter is normally 20 mm and the height is 40 mm. The specimens are first compacted and then saturated in a separate device.

After the specimens are removed from the saturation device the actual test can start. A schematic drawing of the test setup is shown in Figure 16-1. The test is made at a rate of deformation of 0.8 % of the sample height per minute at continuously measurement of the applied load and deformation of the specimen. The unconfined strength is determined as the maximum stress applied to the sample. If no clear maximum in the stress can be determined the strength of the specimen is determined at a strain of 15 %.

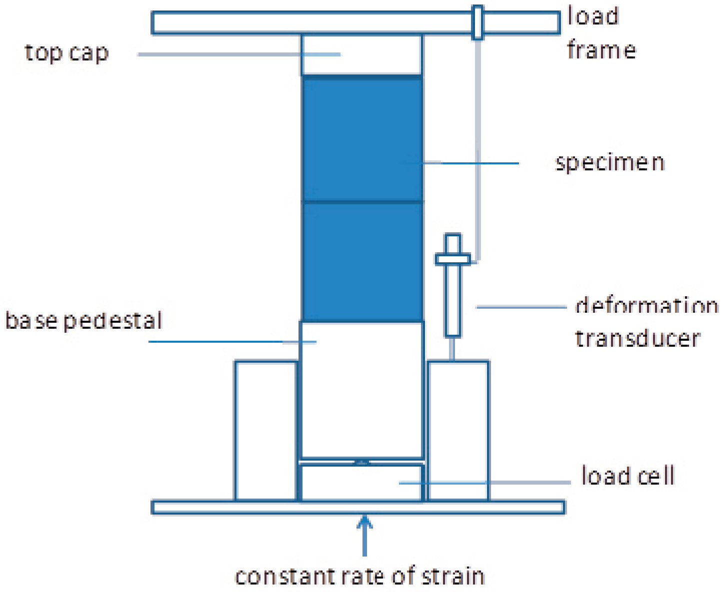

*Figure 16-1. Schematic drawing of the test setup (Dueck et al. 2010).*

After the test, the bulk density is determined by weighting a sample of the specimen both in air and submerged in paraffin oil with known density. The water content is determined by drying a sample in an oven at a temperature of 105 C° for 24 hours. With the known density and water content the dry density of the specimen ($\rho_d$) can be calculated:

$$\rho_d = \frac{\rho}{1+w}$$

## 16.2 Analysis of data

The results used here are described in detail in (Dueck et al. 2010). The determination of the strength is made on specimens of both Ca- and Na-bentonite and the results are presented in Figure 16-2. The Figure shows that at a specified density (or void ratio), the Ca-bentonite has a higher strength compared to a Na-bentonite. It is assumed that the bentonite in a repository will, independent of its initial state, be converted to a Ca-bentonite and thus it is reasonable to state from this data that the bentonite placed around a canister should not have a lower void ratio than about 0.73 (corresponding to a dry density of 1 615 kg/m$^3$), see the red line in Figure 16-2, in order to minimise the unconfined compression strength to 4 000 kPa. Note that the red line in Figure 16-2 is defined on tests made on the bentonite Deponit CaN which is a Ca-dominated bentonite.

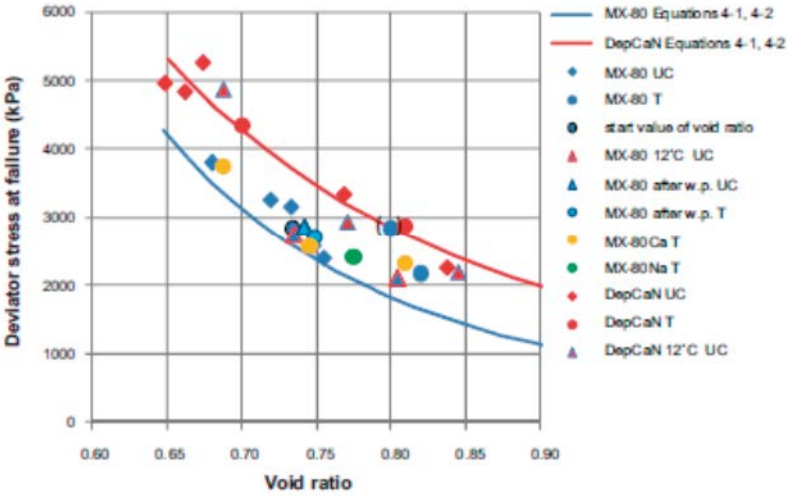

***Figure 16-2.*** *Results from unconfined compression tests (UC) and triaxial tests (T) on MX-80 (blue),MX-80Na (green), MX-80Ca (orange) and DepCaN (red), (Dueck et al. 2010).*

# 17 Compaction properties

Bentonite as highly compacted blocks is used both for the buffer and the backfill in the KBS3-concept for final storage of high level radioactive waste. The compaction is made in rigid moulds with the use of large presses. Water is normally added to the bentonite before the compaction, in order get the right properties of the blocks. The water is added to the bentonite in large mixers. The required properties of the blocks are particularly the dry density of the blocks but also the water content, which is important for an efficient and safe handling, storage and installation of the buffer and backfill blocks. The compaction properties of a bentonite must be investigated before production of blocks can start. The properties vary between different types of bentonites but also between different deliveries of the same bentonite type. The compaction properties for a specific bentonite are preferably investigated in a smaller scale in a laboratory where smaller specimens are compacted at different water contents and at different compaction pressures. The results from the tests are presented as "compaction curves" where the archived dry densities of the specimens are evaluated as function of the compaction pressure and the water content. The results from the tests are used primarily to judge if the bentonite is suitable as material for buffer and/or backfill blocks and thus the test are made as part of the delivery control of the bentonite. The results can also be used for determining suitable compaction pressure and water content for large scale production of bentonite blocks.

## 17.1 Test method

The laboratory test presented is based on tests made during several years of deliveries of bentonite to SKB for production of buffer and backfill blocks. The laboratory test also includes determinations of water content and bulk density of the compacted specimens. These determinations are made in accordance with standard procedures.

The water content for the specimens is varied between 10 % and 26 %. This interval in water content can eventually be changed depending on the initial water content of the bentonite and its ability to hold water. The mixing of water to the decided content is made in the laboratory in steps of 1 percentage point. In total, approximately 1 kg of each mixture, with specified water content, is prepared. It is favourable if the mixed bentonite can be stored in a water tight container or a plastic bag for at least 48 hours in order to get a more homogeneous mixture before the actual compaction of the specimens.

A sample of about 80 g is taken from a mixture and placed in the mould, see Figure 17-1a. The sample is then compacted in a hydraulic press with a maximum load capacity of 20 tonnes, see Figure 17-1b. The diameter of the mould should be 50 mm. This procedure is repeated for each mixture 5 times were the compaction is made with the suggested compaction pressure of 25, 40, 60, 80 and 100 MPa respectively. It might be difficult to reach the highest compaction pressure, 100 MPa, with a mould diameter of 50 mm if the maximum capacity of the press is limited to 20 tonnes and thus a mould with smaller diameter e.g. 35 mm can be used for this compaction pressure. The choice of compaction pressure might be varied due to type of bentonite but it is also depending on whether the bentonite will be used for the backfill or the buffer. The applied load in the press is normally specified in the units tonnes or kN. The calculation of the compaction pressure from the measured load is made as follows:

$$\sigma_{comp} = F \times 4/(\pi D^2) \qquad (17\text{-}1)$$

where

$\sigma_{comp}$ = Compaction pressure (kPa)
F = Applied load (kN)
D = mould diameter (m)

The calculated compaction pressure for two different diameters of the mould is tabulated for different applied load in Table 17-1.

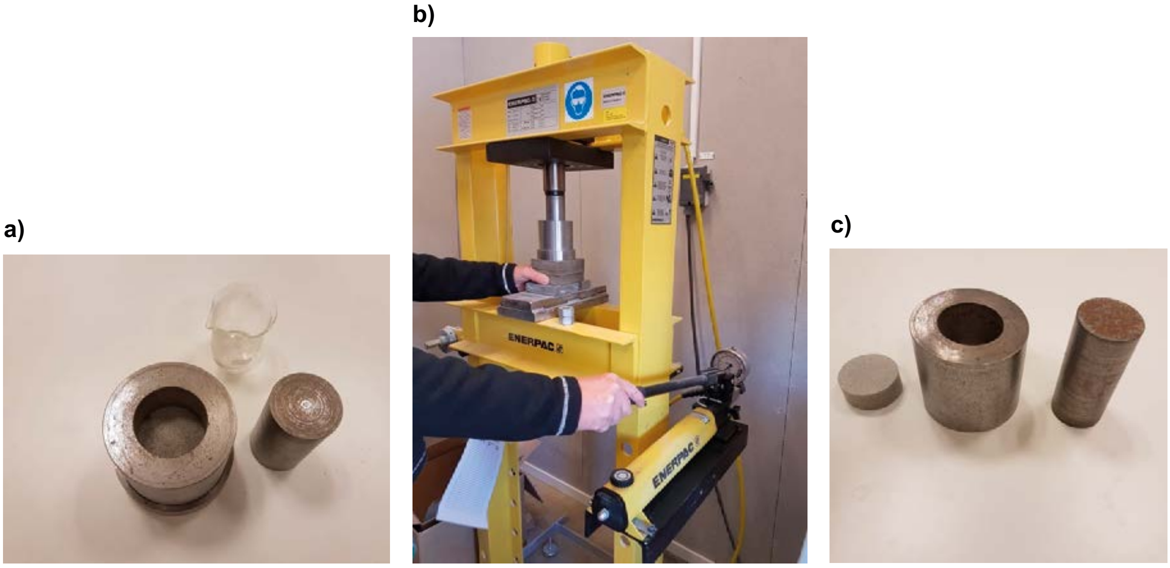

***Figure 17-1.*** *Compaction of bentonite a) the bentonite is filled in the mould, b) the compaction of the specimen made with a hydraulic press, c) the compacted specimen is released from the mould.*

**Table 17-1. The compaction pressure at different diameters of the mould and at different loads.**

| Compaction pressure (MPa) | Diameter mould 50 mm | | Diameter mould 35 mm | |
|---|---|---|---|---|
| | Load (kN) | Load (ton) | Load (kN) | Load (ton) |
| 25 | 49.1 | 5.0 | 24.1 | 2.5 |
| 40 | 78.5 | 8.0 | 38.5 | 3.9 |
| 60 | 117.8 | 12.0 | 57.7 | 5.9 |
| 80 | 157.1 | 16.0 | 77.0 | 7.8 |
| 100 | 196.3 | 20.0 | 96.2 | 9.8 |

## 17.2 Analysis of data

After the compaction, and the density and water content are determined on the specimens, compilations and analysis of the results are made. It is suggested that the dry density of the specimens are plotted as function of both the water content and the applied compaction pressure, see Figure 17-2. The data shown in the figure comes from compaction test made on MX-80. The figure shows that the dry density made at constant compaction pressure is decreasing at an increasing of the water content. There is a tendency that at the lowest compaction pressure (25 MPa) the maximum dry density is reached at a water content of about 0.13, i.e. there is a maximum in the compaction curve. This type of maximum might be more pronounced for other types of bentonite. Furthermore, the figure is showing that the dry density is increasing when the compaction pressure is increasing when the water content is kept constant.

The results from the tests are used for optimising the water content and the compaction pressure at large scale production of buffer and backfill blocks. The most important requirement on the blocks is normally the achievable dry density. In addition to this there might also be requirements on the water content of the blocks in order to minimize the risk of damages during handling, storage and installation.

If, as an example for this bentonite, the requirement on the dry density for the blocks is 1 750 kg/m$^3$ at a water content of 0.17 the blocks should be compacted with a compaction pressure of about 40 MPa.

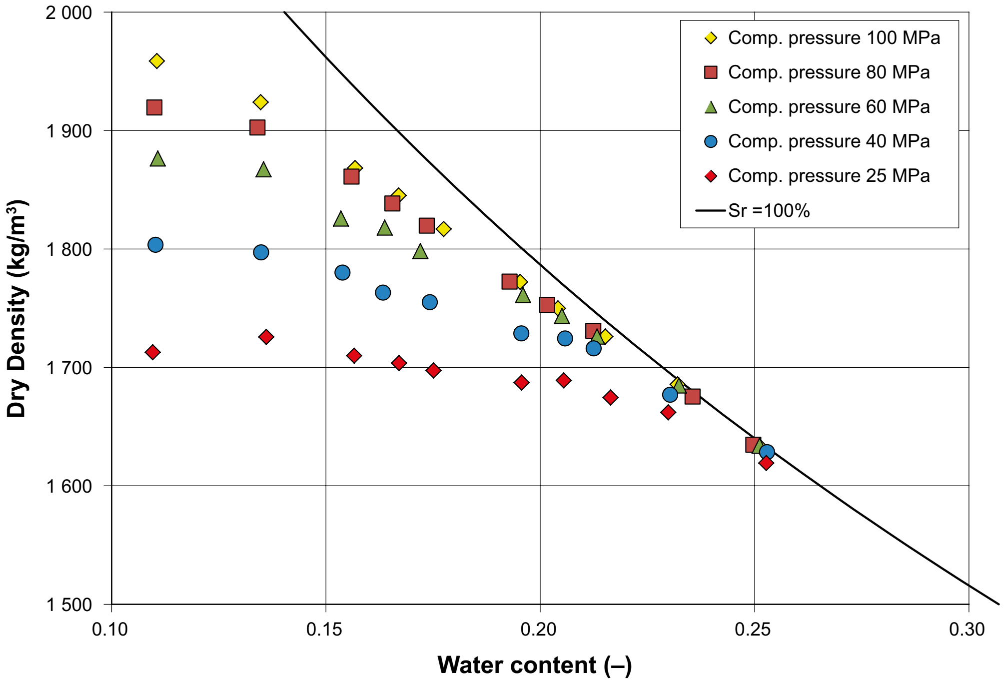

***Figure 17-2.*** *The dry density as function of water content at five different compaction pressures. The compactions are made with MX-80.*

# 18 Analysis of carbon and sulphur

## 18.1 Introduction

Carbon (coal) is in bentonite in the form of inorganic and organic carbon. Exactly which compounds are organic or inorganic is not always obvious. SKB is particularly interested in organic carbon from the perspective of whether it can be an energy source for microbes. Inorganic carbon compounds in the bentonite are especially carbonates (calcite, dolomite, etc.) but the presence of graphite probably cannot be completely excluded. The carbonates are more or less water-soluble and in field tests they sometimes can be seen to accumulate towards a heater. Organic carbon compounds that may be relevant are coal, bitumen and humic substances. Some of the organic carbon compounds are soluble in organic solvent, whereupon they can be extracted from the bentonite and analyzed with for example a gas or liquid chromatograph, which can give qualitative information about the types of compounds present, and thus information on the clay origin and formation environment. Currently, SKB has no requirements on the deeper levels of detail other than that the weight percentage of organic carbon should not exceed 1 percent by weight.

Sulfur is found in bentonite especially as sulphide (pyrite) and sulphate (gypsum), but elemental sulfur and possibly other forms of sulfur cannot be totally excluded. Sulphates are soluble in water and in field experiment are often transported, and enrichments of sulphate against a heater can also be seen. Sulphates are themselves not reactive to the copper canister, but under the right circumstances they can be converted to sulphide by sulphate-reducing bacteria, and therefore sulphates still has some relevance. Water soluble sulfides can attack the copper canister and therefore focus is more on sulphides than on the sulphates. The solubility of sulphides is very low and it is uncertain how well sulphides can be transported in bentonite in gas or liquid.

The design criteria of the bentonite buffer is a maximum of 0.5 percent sulphide (equivalent to about 1 percent pyrite) and 1 percent of total sulfur.

LECO combustion analysis instruments are relatively easy to care for. Normally, service 1 time per year (in 2015 the cost was about 30 000 SEK). The instrument consists of a computer and an oven with IR detector (about 70 × 70 × 80 cm wide). Each measurement takes a few minutes. There's autosampler for 50 samples which costs about 350 000 SEK extra. Automatic weighing is also available as an option. Quantitative determination of the carbon and sulfur can be thermospectrophotometric, i.e. a weighed sample is heated to a high temperature whereupon carbon and sulfur oxidize and depart in gaseous form which is detected spectroscopically, for example by an infrared detector. A standard commercial equipment for this is called LECO. To distinguish between total carbon and organic carbon, analyses always use at least two samples, an initial sample and a pretreated sample where either the organic or the inorganic carbon is chemically or physically removed. Carbonates are removed by acid treatment and heating at 65 °C, while the organic carbon is removed by thermal or chemical oxidation (e.g. hydrogen peroxide, sodium hypochlorite). There are also instruments that will ramp up the temperature for example from 100 to 1 000 °C where organic carbon and inorganic carbon can be determined at the same time if one determines a temperature border. For example, all the carbon dioxide detected over 550 ºC linked to organic carbon (Karnland et al. 2006).

Total sulfur is often analyzed at about 1 200 °C, and a separate sample is analysed by heating at 800 °C where the burning of the sulphides and sulphate alone remains. The amount of sulphide thus calculated as total sulfur – the amount of sulfate (Karnland et al. 2006). There are several very competent suppliers who can do these analyses in a better and more efficient way than SKB. It is therefore recommended that SKB does not itself perform this type of analysis. This document is intended solely to provide information about the practice and to raise awareness of the difficulties and interferences.

Elemental sulfur and sulfur compounds can give a clearly higher sulphide concentration. Graphite may give a seemingly higher content of carbonates. Exactly what temperatures to be selected to oxidise the sulphides without sulphate affected, and to oxidise organic carbon without carbonates affected is a tradeoff. Supplementary analyses reduces uncertainty, e.g. extraction, dissolution with acid or chemical oxidation. Samples may also be fortified with known supplements on the current phase prior to analysis to increase understanding of the test method validity. Graphite in larger amounts (> 1–2 weight percent) can be seen with X-ray diffraction (XRD). XRF also provides total sulfur, but not with the same accuracy. Abnormally high levels of sulfur in the XRF data should be checked up by LECO analysis.

Total carbon, organic carbon and total sulphur for a number of bentonites can be seen in Svensson et al. (2011), regarding organic carbon some bentonites were below detection limit, and the highest was 0.45 wt%, hence all materials were below the allowed limit of 1 wt% (Table 4-1).

Total sulphur in DepCAN was 0.7 wt% while the other bentonites were around 0.3 or lower. Also total sulphur was lower in all bentonites (Svensson et al. 2011) than the accepted 1 wt% (Table 4-1).

Also in Karnland et al. (2006, pp 25–26) plenty of carbon and sulphur data are reported for different bentonites.The highest reported organic carbon content was 0.58 wt%. Sulphide levels for Milos bentonite was in the range of 0.2–0.3 wt%, which is below the 0.5 % level of acceptance (Table 4-1). The Kutch bentonites had very low levels of sulphide, 0.00–0.05 wt%, and the Wyoming bentonites were in the range of 0.04–0.16 wt% sulphide.

## 18.2 Analytical methods

These analysis are currently not performed in house, but instead are done at external laboratories.

Analyses to perform:

- Total carbon and sulphur
- Organic carbon
- Sulphide

The total cost at Acmelab in 2016 was about $ 63 per sample.

# 19 Thermal conductivity

The thermal evolution of the near field in a repository is of importance for the post closure safety of the engineered barriers. In order to avoid mineral transformation of the buffer the maximum temperature in the buffer must not exceed 100 °C.

The thermal evolution of the repository depends on the thermal properties of the canister, rock and buffer, the decay power of the encapsulated spent nuclear fuel and on the canister spacing. For the installed buffer, the thermal evolution will depend on the occurrence and thermal properties of air-filled gaps, and the thermal properties of the buffer blocks and pellet-filled slots. The thermal conductivity of the installed buffer strongly depends on buffer design with blocks and pellets and on its degree of saturation. A saturated buffer has 2–3 times higher thermal conductivity than a dry buffer. In order to analyse the temperature development in the repository, the thermal conductivity of the installed buffer must be known, and how it depends on its density and degree of saturation.

The expected density at saturation for the buffer is approximately 2 000 kg/m$^3$. However, at the saturation and homogenisation of the buffer, both higher and lower densities are expected and thus the used test method for evaluating the thermal conductivity must be suitable for densities at saturation between 1 600–2 020 kg/m$^3$.

## 19.1 Test method

A method for determining the thermal conductivity (λ) is described in the "Standard Test Method for Determination of Thermal Conductivity of Soil and Soft Rock by Thermal Needle Probe Procedure" (ASTM D5334-14). With this method the thermal conductivity is determined by applying a constant power on a needle shaped probe, i.e. the length of the probe is much larger than its diameter, inserted in the centre of a sample. The probe is considered to be a linear heat source. The temperature is measured at mid height of the probe. Beside the probe a device for producing a constant power and a temperature readout unit are needed. Several commercial devices including all the parts are available on the market.

The specimen of buffer material must be prepared in advanced to specified dry densities and water contents. The suitable volume and shape of the samples depends on the dimensions of the probe, the used power and the duration of the test. It is important to prevent large redistributions of water during the test. A hole is drilled in the centre of the sample with a diameter as close as possible to the diameter of the probe.

The water content and density of the specimen is determined after the test.

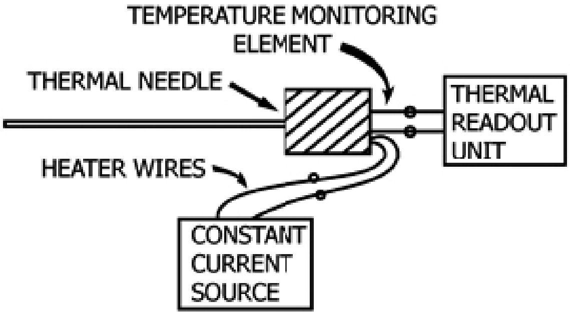

***Figure 19-1.*** *Thermal Probe Experimental Setup (ASTM D5334-14).*

## 19.2 Analyses of data

The temperature increase on the surface of the probe can be calculated according the following (if the probe is considered to be a linear source):

$$\Delta T = -\frac{Q}{4\pi\lambda}E_i\left(\frac{-r^2}{4Dt}\right) \tag{19-1}$$

where

$$E_i(-x) = \int_x^\infty \frac{1}{z}e^{-z}dz \tag{19-2}$$

and

$t$ = time from the beginning of heating (s)
$\Delta T$ = change in temperature from time zero (K)
$Q$ = heat input per unit length of heater (W/m)
$r$ = distance from the heated needle (m)
$D$ = thermal diffusivity ($m^2/s$)
$\lambda$ = thermal conductivity ($W/(m\cdot K)$)

Equation (19-1) can be approximated for high time values to:

$$T_{t2} - T_{t1} = \frac{Q}{4\pi\lambda}ln\frac{t_2}{t_1} \tag{19-3}$$

where

$T_{t1}$ and $T_{t2}$ are temperature values at the times $t_1$ and $t_2$ respectively.

From equation (19-3) the thermal conductivity the thermal conductivity ($\lambda$) can be evaluated as:

$$\lambda = \frac{r^2}{4\pi(T_{t2}-T_{t1})}ln\frac{t_2}{t_1} \tag{19-4}$$

Equation 19-4 implies that the temperature plotted as function of the time in a logarithmic scale curve should be straight line. Performed test on bentonite have shown that this is the case (Börgesson et al. 1994), see Figure 19-2. The figure is indicating that the temperature curve

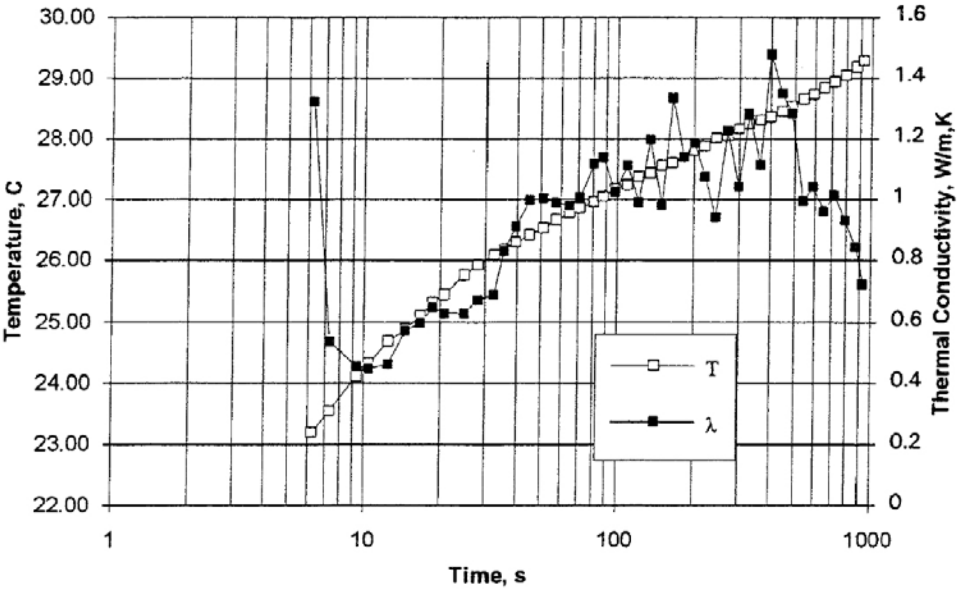

*Figure 19-2. Measured temperature and evaluated thermal conductivity. The test is made on a Na-bentonite with the void ratio e = 1.5 and the degree of saturation Sr = 98 % corresponding to a bulk density of 1 700 kg/m*$^3$ *with a water content of w = 53 %. (Börgesson et al. 1994).*

deviates from the straight line at the beginning of the test, when the properties of the probe and the contact resistance dominate the behaviour, and at the end of the test when the heating front reaches the outer boundary of the specimen. However, the temperature curve in Figure 19-2 is approximately a straight line between 50 s and 500 s. A graphically evaluation of the thermal conductivity with a best fitting line gives in this case a thermal conductivity of $\lambda$ = 1.08 W/m,K. The thermal conductivity is also evaluated at each individual time step in Figure 19-2. Due to the very small time steps and the corresponding small changes in the temperature the evaluated thermal conductivity varies. By doing the evaluation of the thermal conductivity over larger time interval, the variation can be smaller (Börgesson et al. 1994)

# 20 Evaluation of mineralogy and chemistry in bentonite batches over time and detection of contaminants

The purpose of the work reported in this chapter was to evaluate the differences in chemical and mineralogical content with focus on montmorillonite content in seven bentonite batches from Wyoming and Milos by independently using X-ray diffraction (XRD), Cation Exchange Capacity (CEC) and chemical analysis by X-ray fluorescence spectroscopy (XRF). Montmorillonite is the active component in bentonite (swelling clay mineral) therefore, it is important to study how the montmorillonite content varies between different bentonite batches. The target here is to find ways to quantify or correlate each method independently to the montmorillonite content for the specific batches, and later to compare the methods to each other to verify and illustrate how the methods can be used. The absolute values of the montmorillonite content is important in the production of buffer and backfill components, but even more important is a low variation (high homogeneity) within a batch. With more types of analysis data such as exchangeable cations (EC) and chemical data of the clay fractions the analysis could have been done in more detail.

Some of the batches were analysed more extensively than others. One reason for this was the available amount of material that restricted the number of analysis of the 1993 and 2006 MX80 batches.

The measurements were done as described in Chapter 8, 9 and 10. In this section, results from 34 XRD analyses, 200 CEC analyses and 250 XRF analyses were used. Among the CEC analyses 6 values were removed as they were regarded too far away from the mean value. The amount of available bentonite differed between the bentonite types.

Therefore, some of the batches were sampled more extensively and from several bags (MX-80 2012), while other bentonite types were sampled only from a single jar (MX-80 1993, 2006, and DepCAN) and in others a larger jar was homogenised and sampled (MX-80 2002, 2015 and Ibeco BF). This should not be forgotten, and could well be a partly limiting factor in the usefulness of the study.

Regarding XRD the montmorillonite content was estimated using the Siroquant software using a curve fitting approach. Regarding CEC the montmorillonite content was estimated as the ratio of the CEC of the bentonite clay (bulk) and the CEC of the clay fraction (ideally pure montmorillonite, but this is rarely the case). With XRF the strategy to find some sort of correlation for the montmorillonite content was to follow the ratio of the main elements of the montmorillonite (e.g. Mg + Al) divided by the main elements of the accessory minerals (e.g. Si). The choice of elements is dependent on the chemical content of the specific montmorillonite, and the content of the specific accessory minerals. Hence for different bentonites different ratios will work better than others for the approximation. In some bentonites it may work well while in others not at all, and it is important to remember that XRF is not a method for independent montmorillonite quantification, but the high speed and repeatability of XRF compared to CEC or XRD makes it a valuable complement when looking for small differences or when screening large quantities of bentonite.

## 20.1 Wyoming bentonites

The montmorillonite content has been similar and with small variations for the MX80 deliveries throughout the years (Figure 20-1), however, seem to have increased somewhat from approximately 83 to 86 wt% according to the XRD results (Table 20-1). The XRD-data was evaluated with the Rietveld refinement software Siroquant (version 3). This evaluation is based on fitting the data with a theoretical model pattern that is calculated and refined towards the experimental data, iteratively. Qualitative identification of minerals present at a very low level (< 2 %) is difficult and there are several of these phases totally summing up to approximately 5 %. The identification of most of these is based on only one or two of the strongest reflections. Hence, uncertainties are associated with the inclusion or exclusion of these phases,e.g. excluding cristobalite and tridymite increases the apparent montmorillonite content. Since the evaluation of the presented XRD-data in this section is based on the same parameter setup in the evaluation they should be comparable to each other in a higher extent than other analysis performed previously, were different conditions were applied to the different batches.

**Table 20-1. Mineralogy in Wyoming MX-80 batches as determined by XRD/Siroquant. SD(n), n = number of measurements used for calculation of standard deviation.**

| | Montmorillonite | Quartz | Anorthite | Cristobalite | Calcite | Albite | Pyrite | Mica/illite | Gypsum | Tridymite |
|---|---|---|---|---|---|---|---|---|---|---|
| **MX80 2015** | 85.43 | 4.18 | 0.00 | 1.15 | 0.43 | 2.03 | 0.35 | 4.63 | 0.85 | 0.95 |
| SD (4): | 0.73 | 0.38 | 0.00 | 0.10 | 0.10 | 0.26 | 0.06 | 1.52 | 0.40 | 0.06 |
| **MX80 2012** | 86.15 | 4.56 | 0.37 | 0.35 | 0.23 | 1.41 | 0.33 | 5.27 | 0.49 | 0.83 |
| SD (10): | 1.83 | 0.81 | 0.99 | 0.05 | 0.14 | 0.47 | 0.00 | 0.74 | 0.08 | 0.08 |
| **MX80 2006** | 83.9 | 2.7 | 0 | 2.1 | 0.2 | 3.3 | 0.2 | 6 | 0.5 | 1.1 |
| **MX80 2002** | 83.90 | 4.23 | 0.77 | 1.37 | 0.17 | 1.47 | 0.30 | 5.73 | 0.87 | 1.13 |
| SD (3): | 0.85 | 0.15 | 0.83 | 0.12 | 0.21 | 0.42 | 0.00 | 0.40 | 0.12 | 0.06 |
| **MX80 1993** | 82.83 | 3.13 | 0.57 | 1.97 | 0.17 | 3.27 | 0.13 | 5.70 | 0.87 | 1.30 |
| SD (3): | 0.83 | 0.25 | 0.60 | 0.12 | 0.12 | 0.65 | 0.06 | 0.56 | 0.06 | 0.00 |

The MX80 2012 batch has previously been analyzed at another laboratory (Johannesson 2014), and the reported XRD-results indicated similar results as presented in this section, with the main differences of 90 wt% montmorillonite and 1 % mica. The $K_2O$ content was similar in both investigations and support the higher mica and lower montmorillonite contents found in this investigation. Cristobalite was not reported in the evaluated data but identified qualitatively in the XRD data (Johannesson 2014). Identification of cristobalite is difficult as some reflections overlap reflections from feldspar; hence its presence or absence is not trivial.

The CEC results showed the same overall trend between the batches (Figure 20-3) but indicated a somewhat larger difference between the batches (83 to 92 wt%; Table 20-4). The montmorillonite content with the CEC method was approximated by the ratio of the CEC of the sample and the CEC of the pure clay fraction. As the clay fraction was not pure montmorillonite, the CEC of the clay fraction was underestimated; hence the montmorillonite content of the sample was overestimated with this method. The average CEC of the 2012 batch was 84.7 cmol(+)/kg, which is lower than 90, which was reported previously (Johannesson 2014).

The XRF results, especially the Fe content, were found to depend somewhat on whether the samples were milled or not. This is not further commented here, however, the impact was small and one should remember that sample preparation is critical in all methods used (this was not interpreted as that the iron content was affected by the treatment, but the measurement of the iron content).

The structural parts of Wyoming montmorillonite consists of mainly Mg, Al and Si, and the main accessory minerals are dominated by Si with minor Al (Karnland et al. 2006).

Hence, a plot of the (Mg + Al)/Si should correlate fairly well to the montmorillonite content. The ratios of the batches (Figure 20-4) follow a similar pattern as the CEC of the batches (Figure 20-3). Hence, plotting the montmorillonite content obtained from XRD and CEC towards the (Mg+Al)/Si ratio can be a compact way to illustrate and summarise the data (Figure 20-5).

In the 2012 batch the ratio was found to be 0.39, which is very close to 0.38 that can be calculated from reported data (Johannesson 2014). Magnesium is present in the exchangable cations and make up about 8 % of total EC in the 2012 batch, and the variation compared to the other investigated batches is small (Johannesson, 2014). Mg-Wyoming has 3.9 wt% MgO, compared to 2.1 wt% MgO for Ca-Wyoming (Karnland et al. 2006). Hence, at 8 % Mg as interlayer cation, the contribution to total MgO is approximately 0.08 x (3.9–2.1) = 0.14 wt%. This is very small compared to the total $Al_2O_3$+MgO of about 25 wt%, and hence, the variation of EC in MX80 seems to generally have a very small impact on the Mg+Al/Si ratio, but may account for small differences between the batches. This could be further refined with EC data from each batch.

The relation between measured CEC and montmorillonite content from XRD was fairly linear, and the deviation is well within expected uncertainty of the methods (Figure 20-6). Compared to chemical data (Figure 20-5) and CEC (Figure 20-6), it seems that the XRD results of the MX-80 2002 batch possibly underestimated the montmorillonite content somewhat.

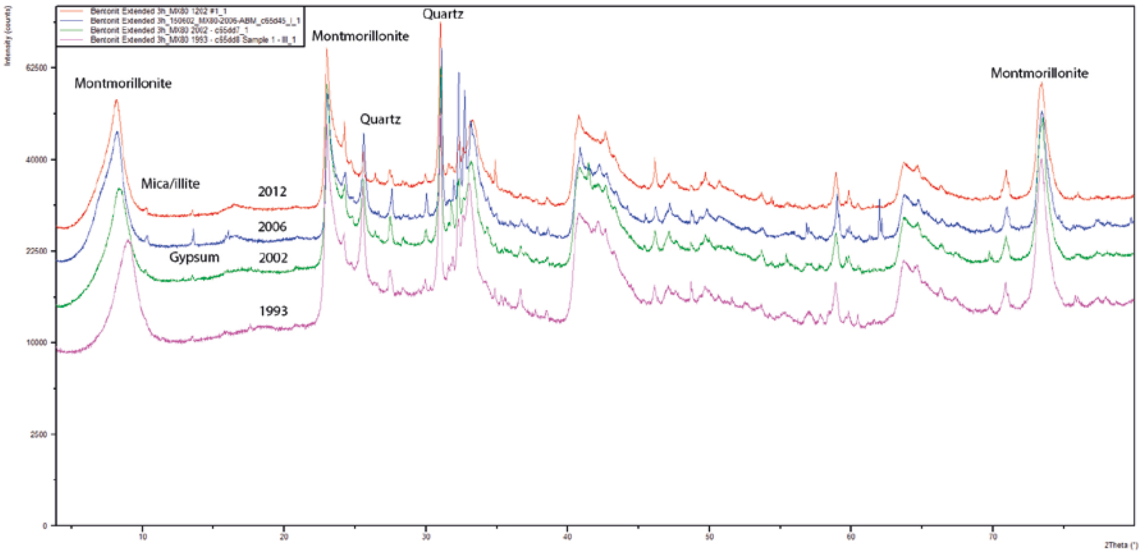

***Figure 20-1.** XRD profiles for the Wyoming bentonites (intensity vs two theta angle).*

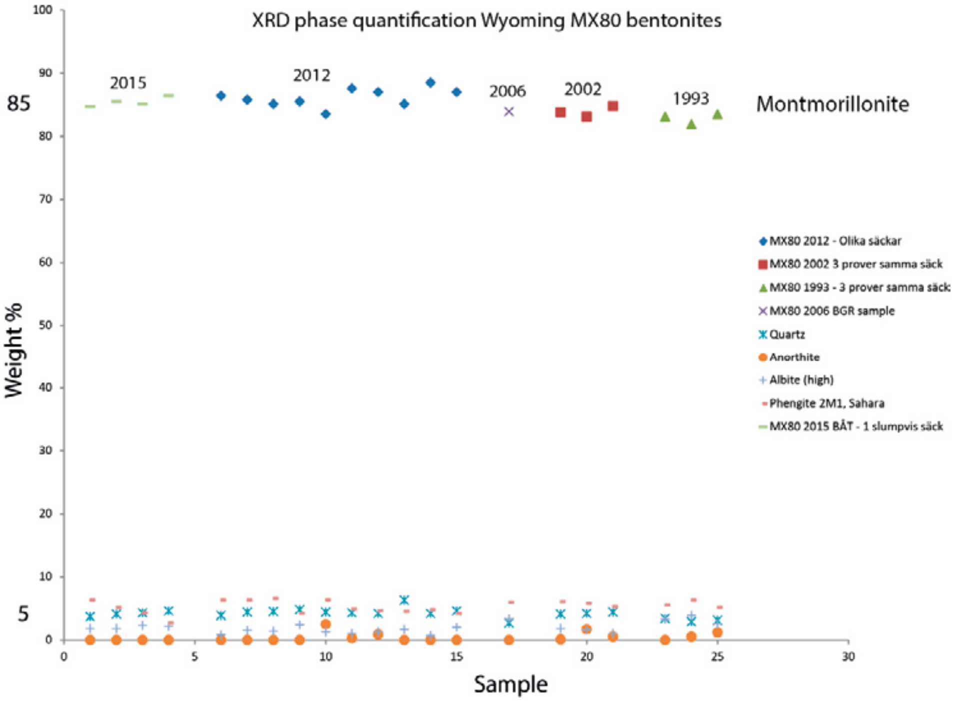

***Figure 20-2.** Phase quantifications with XRD/Siroquant in Wyoming MX-80 bentonites. The years of the delivery of each batch is marked. The main phases are included. Sample number on x-axis.*

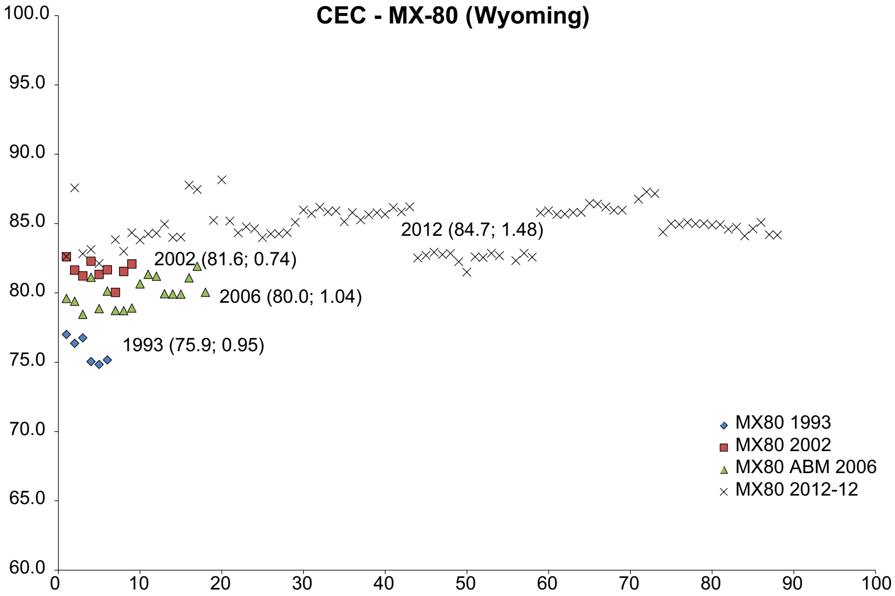

***Figure 20-3.*** *CEC (cmol(+)/kg) in the Wyoming MX-80 bentonites (Cu-tri/UV-vis method). X-axis show sample number.*

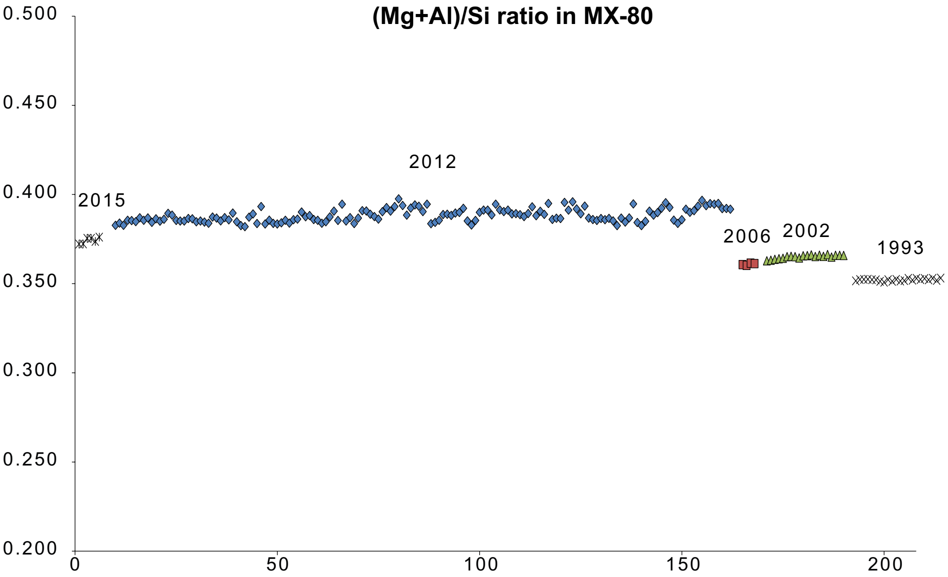

***Figure 20-4.*** *(Mg+Al)/Si ratio in Wyoming MX-80 batches as determined by XRF. Sample number on x-axis.*

If the montmorillonite was identical in all MX80 batches, the different batches were more or less diluted with abundant minerals such as quartz, feldspar and mica. The mineralogy of the batches (Figure 20-2) is qualitatively fairly equal over time regarding the dominant accessory minerals. However, the chemical content of the montmorillonite and its layer charge most likely differ somewhat between shipments. The correlation between the chemical content and montmorillonite content from CEC and XRD is far from perfect between the batches (Figure 20-5), and this also is true also for the correlation of montmorillonite from XRD compared to the CEC (Figure 20-6). However, the spread in data within some of the batches (e.g. 1993) was not negligible, the type of interlayer cations were totally neglected, the bentonites may have been treated differently during the mining, processing (drying temperature) and some of them have been stored for more than 20 years, while others were almost fresh. In Chapter 21, the impact on CEC from many factors are briefly evaluated and described and it is far from trivial.

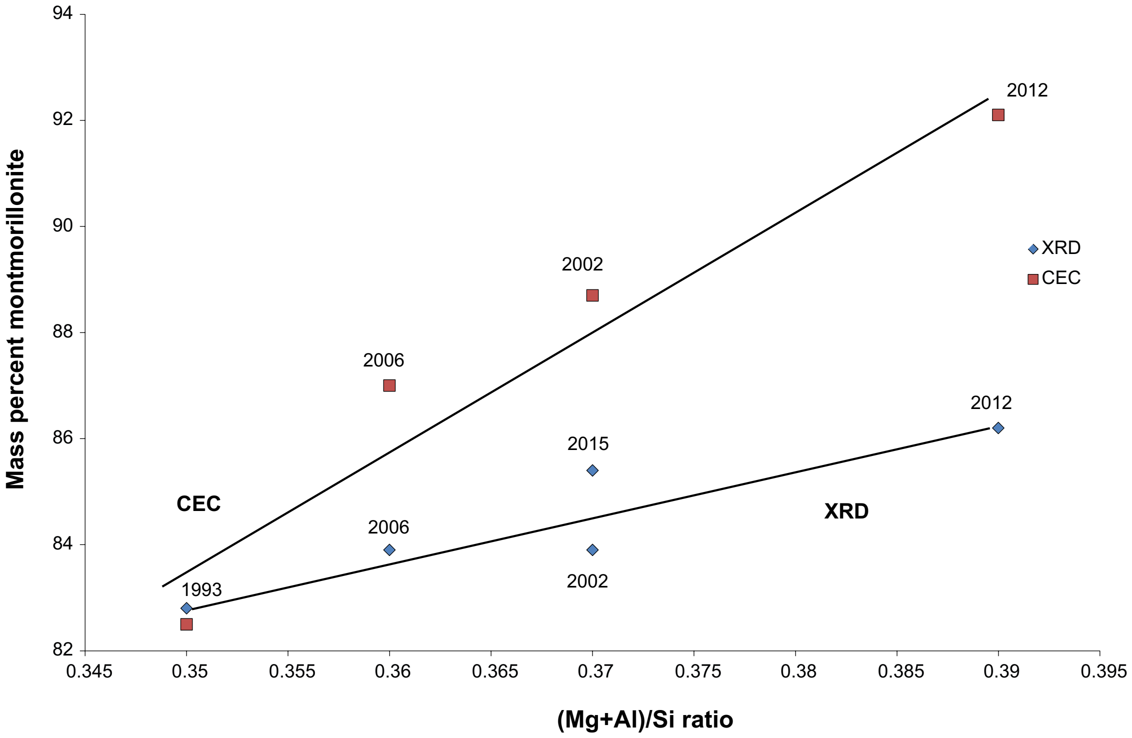

***Figure 20-5.*** *Montmorillonite content (wt%) in MX80 from CEC and XRD as a function of the (Mg+Al)/Si ratio. The lines are provided as guides for the eyes, indicating the trends.*

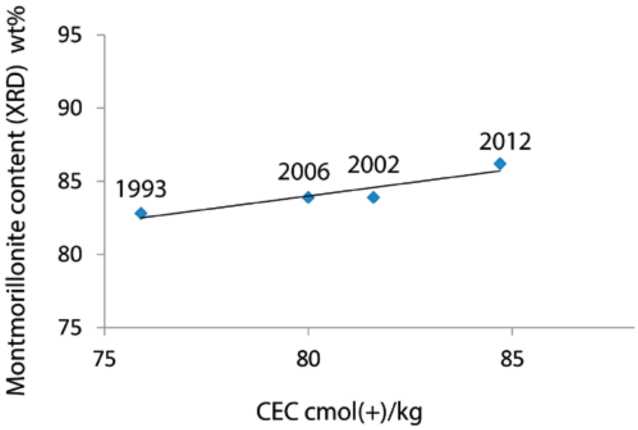

***Figure 20-6.*** *Montmorillonite content (wt%) in the MX80 batches from XRD as a function of the CEC. A linear regression of the line correspond to* $y = 0.3642x + 54.862$, $R^2 = 0.8696$.

## 20.2 Wyoming bentonite – sand mixtures

To better illustrate how the variation in montmorillonite content could look like within a single batch and to illustrate and validate how well various proportions of contaminations can be detected, different proportions of natural sand (mainly quartz, feldspar and mica) or potassium feldspar (microcline perthite, Kråkemåla, Småland, Sweden) were added and mixed with the bentonite (0, 1, 5 and 10 wt%; Figure 20-7). With only one measured sample (XRF) the detection of 1 % of sand was not possible , but when averaging 3–4 samples it was possible to detect 1 % of added sand in this example by studying the (Mg+Al)/Si ratio change (Figure 20-7a). When adding feldspar, the impact on the chemistry is stronger and the detection of 1 wt% could be done with only one measurement in this example (Figure 20-7b) using the same procedure. The change for feldspar would be even clearer if potassium was also introduced in the evaluation (ratio), however, the current expression treats sand and feldspar more equally, making the data easier to interpret (use). But of course, a significant change in any of the analysed elements suggests a contamination (variation) that needs a look up. The detailed chemical information and their statistics are seen in Table 20-2 and Table 20-3. By using the chemical composition of the pure bentonite and the pure sand, the composition of the mixtures were calculated and compared to the observed data (Figure 20-7b) and they correlated very well. A contamination of the MX80 bentonite with as little as 1 wt% of sand or feldspar could be detected with the XRF-method, using 1 to 4 datasets to get good enough statistics. Hence the XRF method is expected to be very well suited for homogenisation control of the bentonite to assure low variance in the chemical and mineralogical content.

The bentonite, sand and the same blends were also analysed with XRD (Figure 20-8). By looking at the montmorillonite content, a dilution by 1 % of sand could not be detected by using a single measurement in this example. Possibly several measured samples and/or improved evaluation of the data could have made this possible. However, a 5 % addition of sand was easily detected, decreasing the montmorillonite content from 82.5 to 76.8 wt%. The amount of the main mineral phases (montmorillonite, quartz and anorthite) were calculated for the blends by interpolation of data from the pure bentonite and sand, and fitted well in most cases with the observed data (Figure 20-8; red points).

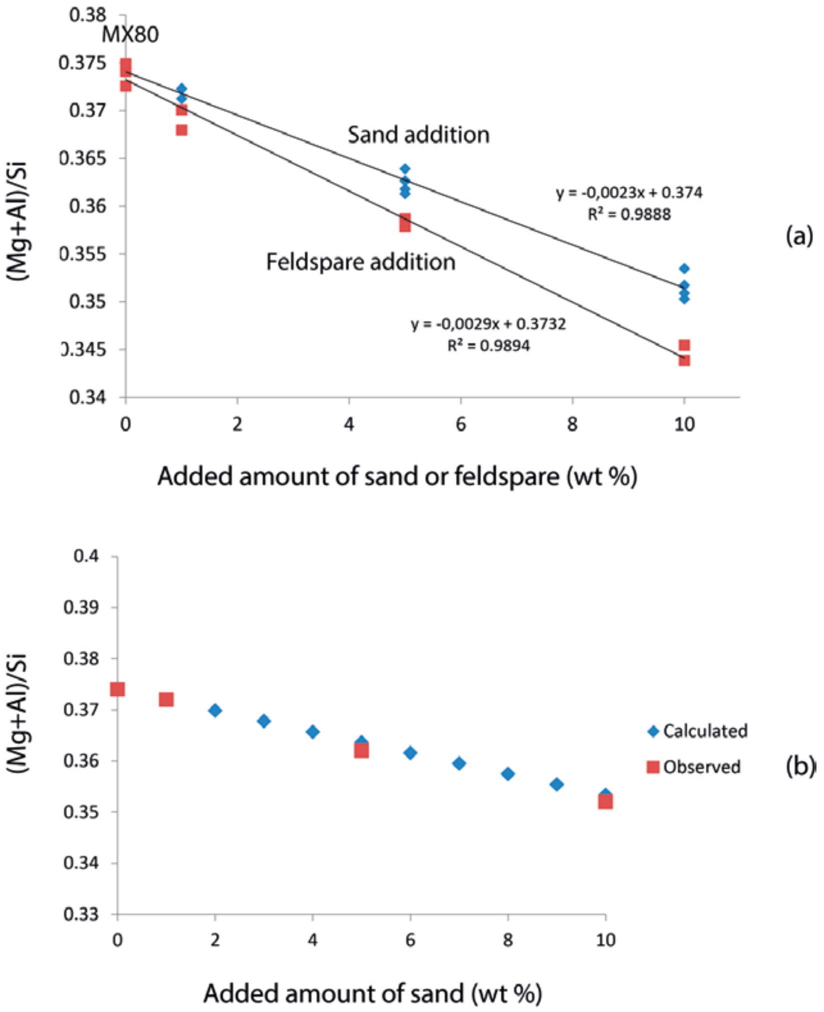

***Figure 20-7.*** *XRF data from the MX-80 2015 batch when blended with milled natural sand or potassium feldspar. (a) The (Mg+Al)/Si ratio as a function of the amount of added sand or feldspar. (b) The observed (Mg+Al)/Si ratio compared to the calculated ratio based on the chemical content of the bentonite and the sand.*

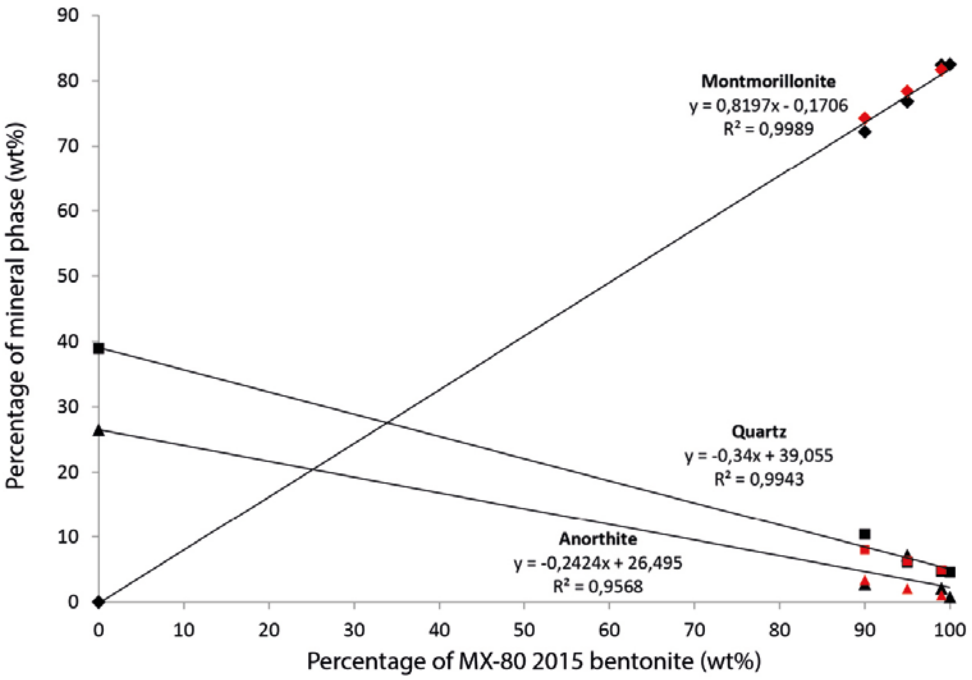

***Figure 20-8.*** *Evaluated XRD data from the MX-80 2015 batch when blended with milled natural sand, showing three selected main minerals and how the vary with the percentage of bentonite in the blend. Red points are calculated by interpolation of the end members (pure bentonite and sand). Data points represent single measurements. 0 % bentonite represent 100 % sand on the X-axis.*

**Table 20-2. Chemical content of MX80 2015 with 0, 1, 5 and 10 wt% of added natural quartz (Q) dominated sand. SD is calculated standard deviation.**

| Sample | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | Cl | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | (Mg+Al)/Si |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **MX80** | 1.804 | 2.407 | 22.135 | 65.874 | 0.004 | 0.589 | 0.012 | 0.619 | 1.622 | 0.205 | 0.016 | 4.714 | 0.373 |
| **MX80** | 1.795 | 2.432 | 22.284 | 66.006 | 0.004 | 0.512 | 0.009 | 0.598 | 1.525 | 0.202 | 0.014 | 4.617 | 0.374 |
| **MX80** | 1.787 | 2.423 | 22.210 | 65.845 | 0.004 | 0.591 | 0.005 | 0.613 | 1.639 | 0.203 | 0.017 | 4.664 | 0.374 |
| **MX80** | 1.786 | 2.427 | 22.251 | 65.821 | 0.007 | 0.554 | 0.008 | 0.619 | 1.659 | 0.203 | 0.016 | 4.650 | 0.375 |
| Average: | 1.793 | 2.422 | 22.220 | 65.887 | 0.005 | 0.562 | 0.009 | 0.612 | 1.611 | 0.203 | 0.016 | 4.661 | **0.374** |
| SD: | 0.008 | 0.011 | 0.064 | 0.083 | 0.002 | 0.037 | 0.003 | 0.010 | 0.059 | 0.001 | 0.001 | 0.040 | 0.001 |
| | | | | | | | | | | | | | |
| **MX80 + 1 % Q** | 1.835 | 2.397 | 22.086 | 65.953 | 0.005 | 0.574 | 0.017 | 0.672 | 1.614 | 0.202 | 0.015 | 4.630 | 0.371 |
| **MX80 + 1 % Q** | 1.831 | 2.406 | 22.168 | 66.015 | 0.005 | 0.531 | 0.007 | 0.641 | 1.582 | 0.201 | 0.017 | 4.597 | 0.372 |
| **MX80 + 1 % Q** | 1.798 | 2.406 | 22.158 | 65.981 | 0.004 | 0.577 | 0.007 | 0.679 | 1.547 | 0.205 | 0.016 | 4.621 | 0.372 |
| **MX80 + 1 % Q** | 1.813 | 2.402 | 22.173 | 66.012 | 0.005 | 0.550 | 0.004 | 0.671 | 1.566 | 0.202 | 0.017 | 4.585 | 0.372 |
| Average: | 1.819 | 2.403 | 22.146 | 65.990 | 0.005 | 0.558 | 0.009 | 0.666 | 1.577 | 0.203 | 0.016 | 4.608 | **0.372** |
| SD: | 0.017 | 0.004 | 0.041 | 0.029 | 0.001 | 0.022 | 0.006 | 0.017 | 0.028 | 0.002 | 0.001 | 0.021 | 0.001 |
| | | | | | | | | | | | | | |
| **MX80 + 5 % Q** | 1.903 | 2.323 | 21.733 | 66.107 | 0.012 | 0.567 | 0.007 | 0.829 | 1.636 | 0.213 | 0.017 | 4.653 | 0.364 |
| **MX80 + 5 % Q** | 1.873 | 2.305 | 21.673 | 66.280 | 0.008 | 0.535 | 0.010 | 0.843 | 1.666 | 0.209 | 0.021 | 4.578 | 0.362 |
| **MX80 + 5 % Q** | 1.863 | 2.278 | 21.556 | 65.969 | 0.011 | 0.511 | 0.009 | 0.876 | 1.692 | 0.217 | 0.018 | 5.001 | 0.361 |
| **MX80 + 5 % Q** | 1.901 | 2.302 | 21.774 | 66.393 | 0.010 | 0.546 | 0.008 | 0.839 | 1.538 | 0.212 | 0.015 | 4.461 | 0.363 |
| Average: | 1.885 | 2.302 | 21.684 | 66.187 | 0.010 | 0.540 | 0.009 | 0.847 | 1.633 | 0.213 | 0.018 | 4.673 | 0.362 |
| SD: | 0.020 | 0.018 | 0.095 | 0.187 | 0.002 | 0.023 | 0.001 | 0.020 | 0.067 | 0.003 | 0.003 | 0.232 | 0.001 |
| | | | | | | | | | | | | | |
| **MX80 + 10 % Q** | 1.947 | 2.235 | 21.348 | 66.724 | 0.016 | 0.525 | 0.008 | 0.994 | 1.556 | 0.206 | 0.016 | 4.424 | 0.353 |
| **MX80 + 10 % Q** | 1.956 | 2.232 | 21.234 | 66.721 | 0.012 | 0.530 | 0.007 | 1.036 | 1.617 | 0.216 | 0.016 | 4.423 | 0.352 |
| **MX80 + 10 % Q** | 1.979 | 2.194 | 21.210 | 66.817 | 0.015 | 0.494 | 0.006 | 1.022 | 1.617 | 0.210 | 0.018 | 4.418 | 0.350 |
| **MX80 + 10 % Q** | 1.894 | 2.219 | 21.184 | 66.699 | 0.017 | 0.537 | 0.010 | 1.029 | 1.702 | 0.219 | 0.019 | 4.470 | 0.351 |
| Average: | 1.944 | 2.220 | 21.244 | 66.740 | 0.015 | 0.522 | 0.008 | 1.020 | 1.623 | 0.213 | 0.017 | 4.434 | **0.352** |
| SD: | 0.036 | 0.019 | 0.072 | 0.052 | 0.002 | 0.019 | 0.002 | 0.018 | 0.060 | 0.006 | 0.002 | 0.024 | 0.001 |

**Table 20-3. Chemical content of MX80 2012 with 0, 1, 5 and 10 wt% of added potassium feldspar (F). SD is calculated standard deviation.**

| Sample | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | Cl | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | (Mg+Al)/Si |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **MX80** | 1.804 | 2.407 | 22.135 | 65.874 | 0.004 | 0.589 | 0.012 | 0.619 | 1.622 | 0.205 | 0.016 | 4.714 | 0.373 |
| **MX80** | 1.795 | 2.432 | 22.284 | 66.006 | 0.004 | 0.512 | 0.009 | 0.598 | 1.525 | 0.202 | 0.014 | 4.617 | 0.374 |
| **MX80** | 1.787 | 2.423 | 22.210 | 65.845 | 0.004 | 0.591 | 0.005 | 0.613 | 1.639 | 0.203 | 0.017 | 4.664 | 0.374 |
| **MX80** | 1.786 | 2.427 | 22.251 | 65.821 | 0.007 | 0.554 | 0.008 | 0.619 | 1.659 | 0.203 | 0.016 | 4.650 | 0.375 |
| Average: | 1.793 | 2.422 | 22.220 | 65.887 | 0.005 | 0.562 | 0.009 | 0.612 | 1.611 | 0.203 | 0.016 | 4.661 | **0.374** |
| SD: | 0.008 | 0.011 | 0.064 | 0.083 | 0.002 | 0.037 | 0.003 | 0.010 | 0.059 | 0.001 | 0.001 | 0.040 | 0.001 |
| | | | | | | | | | | | | | |
| **MX80 + 1 % F** | 1.796 | 2.332 | 21.922 | 65.911 | 0.004 | 0.568 | 0.013 | 0.811 | 1.614 | 0.208 | 0.019 | 4.802 | 0.368 |
| **MX80 + 1 % F** | 1.809 | 2.370 | 22.049 | 65.982 | 0.004 | 0.559 | 0.006 | 0.764 | 1.587 | 0.204 | 0.018 | 4.647 | 0.370 |
| Average: | 1.803 | 2.351 | 21.986 | 65.947 | 0.004 | 0.564 | 0.010 | 0.788 | 1.601 | 0.206 | 0.019 | 4.725 | **0.369** |
| SD: | 0.009 | 0.027 | 0.090 | 0.050 | 0.000 | 0.006 | 0.005 | 0.033 | 0.019 | 0.003 | 0.001 | 0.110 | 0.001 |
| | | | | | | | | | | | | | |
| **MX80 + 5 % F** | 1.874 | 2.197 | 21.522 | 66.274 | 0.006 | 0.558 | 0.014 | 1.353 | 1.516 | 0.189 | 0.015 | 4.482 | 0.358 |
| **MX80 + 5 % F** | 1.849 | 2.198 | 21.532 | 66.280 | 0.005 | 0.514 | 0.013 | 1.358 | 1.535 | 0.195 | 0.016 | 4.505 | 0.358 |
| **MX80 + 5 % F** | 1.874 | 2.198 | 21.584 | 66.300 | 0.006 | 0.529 | 0.008 | 1.341 | 1.510 | 0.196 | 0.015 | 4.439 | 0.359 |
| **MX80 + 5 % F** | 1.884 | 2.188 | 21.543 | 66.207 | 0.005 | 0.598 | 0.010 | 1.363 | 1.533 | 0.194 | 0.018 | 4.460 | 0.358 |
| Average: | 1.870 | 2.195 | 21.545 | 66.265 | 0.006 | 0.550 | 0.011 | 1.354 | 1.524 | 0.194 | 0.016 | 4.472 | **0.358** |
| SD: | 0.015 | 0.005 | 0.027 | 0.040 | 0.001 | 0.037 | 0.003 | 0.009 | 0.012 | 0.003 | 0.001 | 0.028 | 0.000 |
| | | | | | | | | | | | | | |
| **MX80 + 10 % F** | 1.984 | 1.944 | 20.941 | 66.552 | 0.004 | 0.512 | 0.006 | 2.063 | 1.471 | 0.187 | 0.015 | 4.321 | 0.344 |
| **MX80 + 10 % F** | 1.943 | 1.988 | 21.035 | 66.645 | 0.003 | 0.489 | 0.010 | 1.993 | 1.432 | 0.182 | 0.014 | 4.265 | 0.345 |
| Average: | 1.964 | 1.966 | 20.988 | 66.599 | 0.004 | 0.501 | 0.008 | 2.028 | 1.452 | 0.185 | 0.015 | 4.293 | **0.345** |
| SD: | 0.029 | 0.031 | 0.066 | 0.066 | 0.001 | 0.016 | 0.003 | 0.049 | 0.028 | 0.004 | 0.001 | 0.040 | 0.001 |

## 20.3 Milos bentonites

The XRD raw data is seen in Figure 20-9. Both batches of Ibeco BF from Milos had approximately 58–59 wt% montmorillonite according to XRD-data (Figure 20-6, Table 20-4) and 60–61 wt% according to CEC-data (Table 20-6). The high-quality (high montmorillonite) Milos bentonite DepCAN was markedly higher at 80 wt% (XRD), this material was however never intended as a backfill material but instead intended as a buffer candidate material. No separate clay fraction was prepared from the DepCAN and hence, the calculated montmorillonite content from the CEC uses the clay fraction data from the Ibeco BF, and the calculated 76 % was therefore put within parenthesis.

With Wyoming bentonite the (Mg + Al)/Si ratio was found to correlate rather well with the montmorillonite content (Figure 20-5). However, in the case of Ibeco BF clays, this was not the case (cf. Figure 20-10 and Figure 20-12). Among other things, the Ibeco clays contained dolomite ($CaMg(CO_3)_2$), hence Mg could not be used to track the montmorillonite content in this clay, and due to the high dolomite content (XRD; Table 20-4), Mg was omitted. And as ankerite was also observed (XRD; Figure 20-2), Fe was added, and instead the Al/(Si+Fe) ratio was evaluated, and seemed to work somewhat better to capture the montmorillonite trend (cf. Figure 20-13 and Figure 20-10). These bentonite materials are too different to each other to really get much information when comparing their chemical content. The relation between the montmorillonite content from XRD and measured CEC is seen in Figure 20-14.

**Table 20-4. Mineralogy in the Milos bentonite batches as determined by XRD/Siroquant. SD(n), n = number of measurements used for calculation of standard deviation.**

| | Montmo-rillonite | Quartz | Anorthite | Cristo-balite | Calcite 1 | Albite | Pyrite | Mica/illite | Gypsum | Tridymite | Dolomite | Ortho-clase | Ankerite |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Ibeco BF 2004** | 57.92 | 0.45 | 0.00 | 0.00 | 6.67 | 1.77 | 0.38 | 3.35 | 0.00 | 0.05 | 21.12 | 3.73 | 4.60 |
| SD (7): | 3.30 | 0.25 | 0.00 | 0.00 | 3.13 | 1.23 | 0.23 | 1.16 | 0.00 | 0.11 | 1.41 | 0.48 | 1.84 |
| **Ibeco BF 2011** | 58.50 | 0.63 | 0.36 | 0.70 | 4.80 | 2.43 | 0.46 | 4.61 | 0.00 | 0.71 | 26.20 | 0.61 | 0.00 |
| SD (7): | 1.46 | 0.19 | 0.57 | 0.06 | 0.93 | 0.35 | 0.05 | 0.45 | 0.00 | 0.11 | 1.91 | 0.18 | 0.00 |
| **Dep CAN 2006** | 79.90 | 0.87 | 0.00 | 0.67 | 7.00 | 1.33 | 0.70 | 4.50 | 0.77 | 1.30 | 1.03 | 1.90 | 0.03 |
| SD (3): | 0.40 | 0.15 | 0.00 | 0.06 | 0.56 | 0.31 | 0.00 | 0.36 | 0.12 | 0.00 | 0.65 | 0.52 | 0.06 |

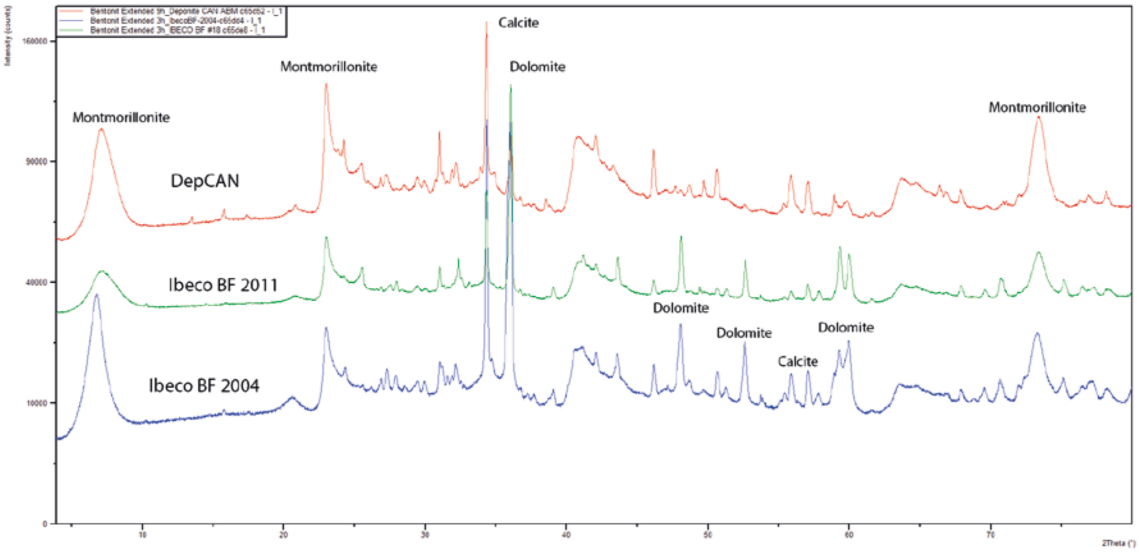

*Figure 20-9. Example of XRD data for the Milos batches (intensity vs two theta angle).*

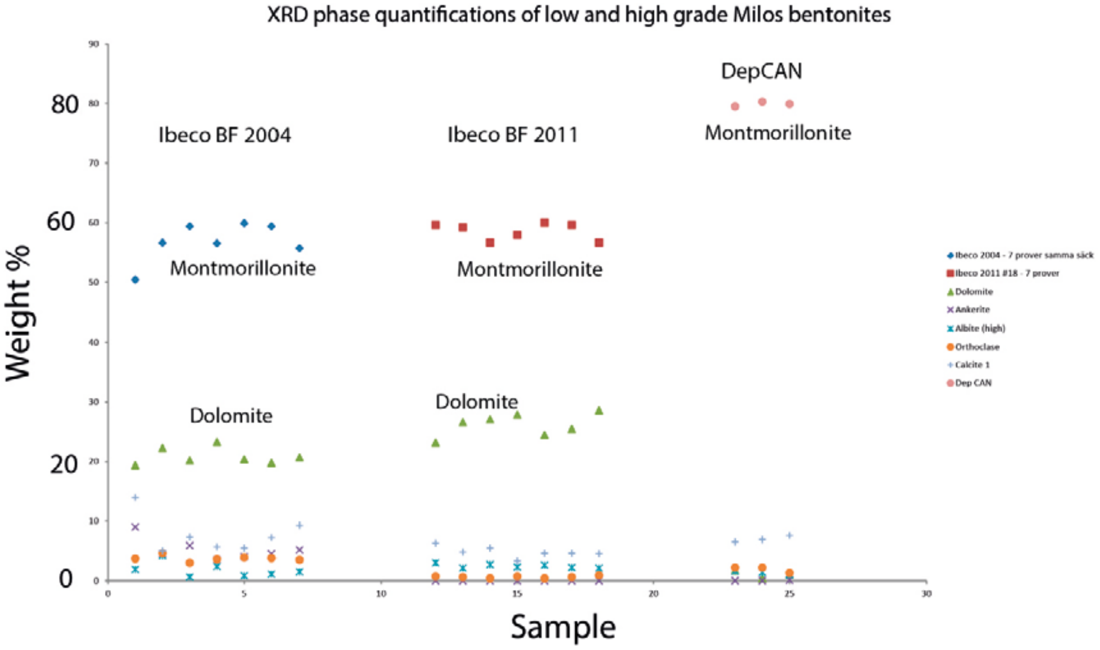

*Figure 20-10. Montmorillonite and main accessory minerals in Milos bentonite batches as determined by XRD/Siroquant.*

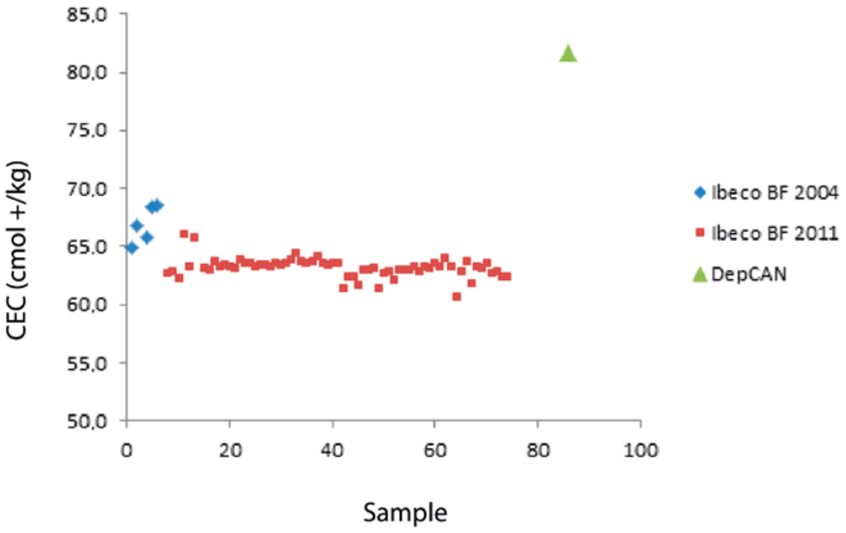

***Figure 20-11.*** *CEC in the Milos bentonite batches (Cu-tri/UV-vis method).*

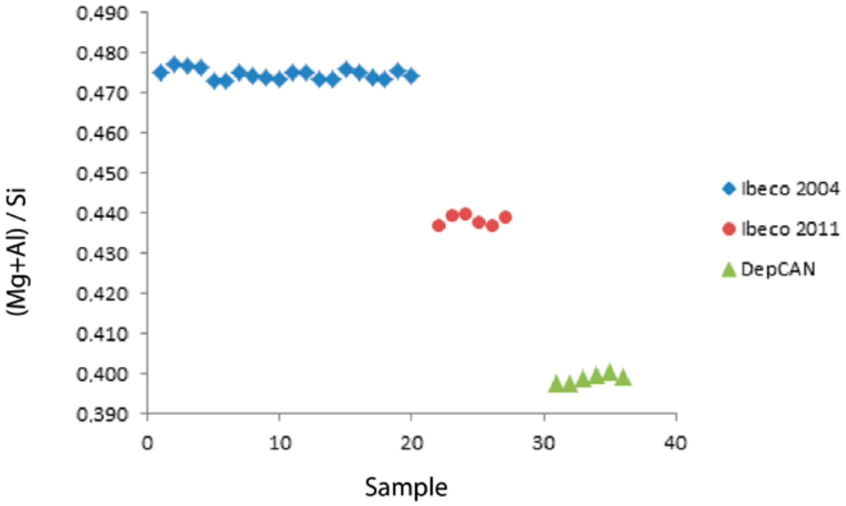

***Figure 20-12.*** *(Mg+Al)/Si ratio in the Milos bentonite batches as determined by XRF.*

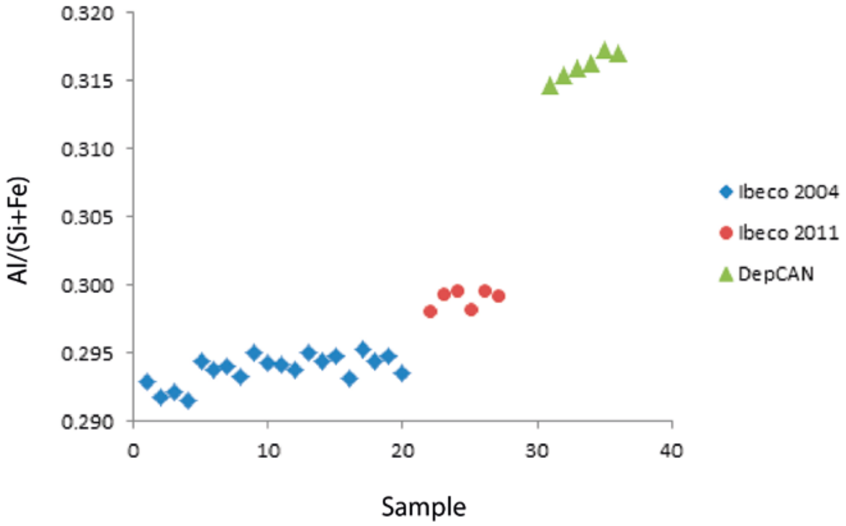

***Figure 20-13.*** *Al/(Si+Fe) ratio in the Milos bentonite batches as determined by XRF.*

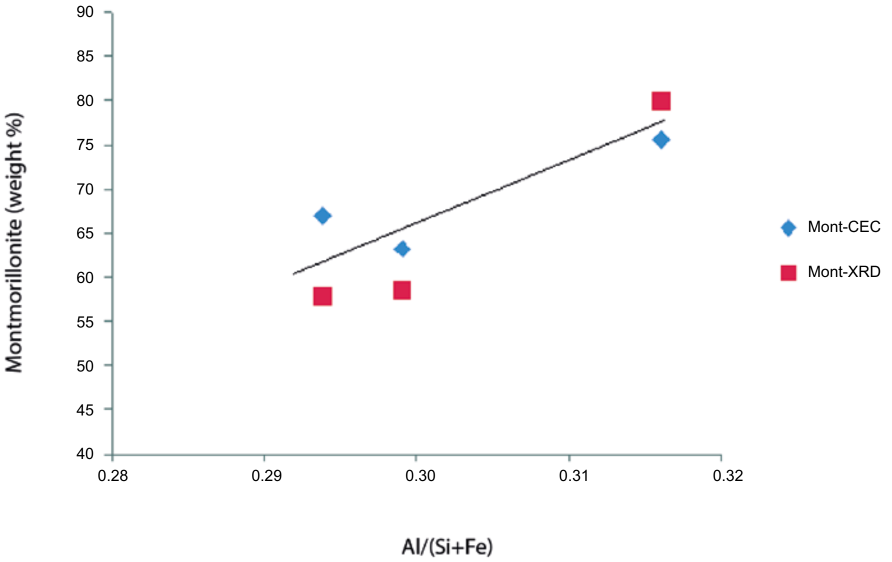

***Figure 20-14.*** *Montmorillonite content in Milos bentonite from CEC and XRD as a function of the Al/(Si+Fe) ratio. The line was provided as a guide for the eyes, indicating the weak trend between the rather different bentonites.*

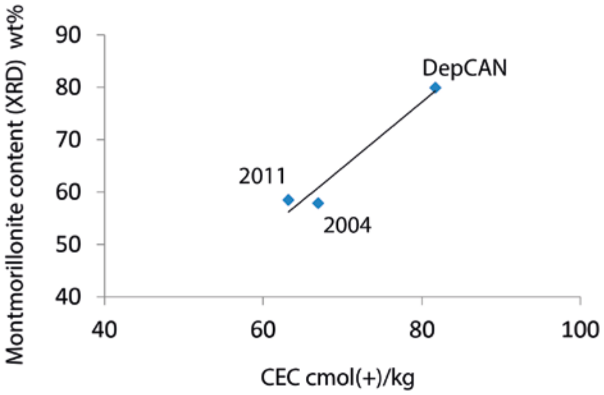

***Figure 20-15.*** *Montmorillonite content (wt%) in the Milos batches from XRD as a function of the CEC. A linear regression of the line correspond to y = 1.251x–22.885; R² = 0.9549.*

**Table 20-5. Overview of the chemical content in the bentonite batches.**

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $Fe_2O_3$ | $P_2O_5$ | $SO_3$ | Cl | $K_2O$ | CaO | $TiO_2$ | MnO |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MX80 2015 | 1.87 | 2.44 | 22.28 | 66.09 | 4.39 | 0.00 | 0.58 | 0.01 | 0.59 | 1.54 | 0.19 | 0.01 |
| | 0.03 | 0.01 | 0.05 | 0.15 | 0.03 | 0.00 | 0.02 | 0.00 | 0.01 | 0.08 | 0.00 | 0.00 |
| MX80 2012 | 1.91 | 2.59 | 22.42 | 64.44 | 4.95 | 0.02 | 0.81 | 0.01 | 0.72 | 1.86 | 0.25 | 0.02 |
| | 0.05 | 0.05 | 0.36 | 0.42 | 0.33 | 0.02 | 0.13 | 0.01 | 0.08 | 0.33 | 0.06 | 0.01 |
| MX80 2006 | 1.67 | 2.52 | 21.55 | 66.71 | 4.35 | 0.01 | 0.83 | 0.01 | 0.55 | 1.60 | 0.18 | 0.01 |
| | 0.04 | 0.02 | 0.02 | 0.06 | 0.05 | 0.00 | 0.07 | 0.00 | 0.04 | 0.06 | 0.01 | 0.00 |
| MX80 2002 | 1.56 | 2.45 | 21.87 | 66.64 | 4.75 | 0.00 | 0.46 | 0.00 | 0.46 | 1.66 | 0.14 | 0.01 |
| | 0.02 | 0.01 | 0.04 | 0.05 | 0.02 | 0.00 | 0.01 | 0.00 | 0.01 | 0.02 | 0.00 | 0.00 |
| MX80 1993 | 1.69 | 2.33 | 21.32 | 67.21 | 4.93 | 0.01 | 0.41 | 0.01 | 0.52 | 1.39 | 0.16 | 0.01 |
| | 0.02 | 0.02 | 0.03 | 0.04 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 |
| Dep CAN 2006 | 0.65 | 3.18 | 20.82 | 60.17 | 5.71 | 0.04 | 1.30 | 0.11 | 1.21 | 5.77 | 0.97 | 0.08 |
| | 0.02 | 0.02 | 0.06 | 0.08 | 0.05 | 0.00 | 0.03 | 0.01 | 0.01 | 0.09 | 0.01 | 0.00 |
| Ibeco BF 2004 | 0.02 | 6.23 | 16.91 | 48.76 | 8.80 | 0.04 | 0.05 | 0.01 | 1.31 | 16.84 | 0.82 | 0.21 |
| | 0.01 | 0.05 | 0.11 | 0.25 | 0.07 | 0.00 | 0.00 | 0.00 | 0.01 | 0.23 | 0.01 | 0.00 |
| Ibeco BF 2011 | 0.73 | 5.51 | 18.19 | 54.03 | 6.78 | 0.03 | 0.17 | 0.05 | 0.80 | 12.65 | 0.82 | 0.24 |
| | 0.01 | 0.04 | 0.05 | 0.12 | 0.03 | 0.00 | 0.00 | 0.00 | 0.02 | 0.10 | 0.00 | 0.00 |

**Table 20-6. Overview of the montmorillonite content in the bentonite batches. SD(n), n = number of measurements used for calculation of standard deviation.**

| Bentonit | Mont. Wt% (XRD) | SD (n) | CEC | SD (n) | Mont. Wt% (CEC) | (Al+Mg)/Si |
|---|---|---|---|---|---|---|
| Wyoming MX80 1993 | 82.8 | 1.8 (3) | 75.9 | 0.95 (6) | 82.5 | 0.35 |
| Wyoming MX80 2002 | 83.9 | 0.9 (3) | 81.6 | 0.74 (9) | 88.7 | 0.37 |
| Wyoming MX80 2006 | 83.9 | | 80 | 1.04 (18) | 87 | 0.36 |
| Wyoming MX80 2012 | 86.2 | 0.8 (10) | 84.7 | 1.48 (88) | 92.1 | 0.39 |
| Wyoming MX80 2015 | 85.4 | 0.7 (4) | | | | 0.37 |
| Milos Ibeco BF 2004 | 57.9 | 3.3 (7) | 66.9 | 1.59 (6) | 60.8 | |
| Milos Ibeco BF 2011 | 58.5 | 1.5 (7) | 63.2 | 0.83 (67) | 59.6 | |
| Milos Dep CAN 2006 | 79.9 | 0.4 (3) | 81.7 | | (75.6) | |

## 20.4 Summary of characterisation

There is currently no quick, simple and reliable method for determining the montmorillonite content in bentonites. Both XRD and CEC are good methods, however, each method has its limitations. With time they will most likely get more optimised and even more refined procedures are expected to be developed. The idea in this work was to use the methods as independently from each other as possible, and to compare trends.

XRD gave information about the accessory minerals present, but amorphous phases may be present and missed as an internal standard (e.g. $Al_2O_3$) was not used in this case. This can be done, however, careful and precise mixing is then needed and knowledge about the exact water content would also be needed for all samples. This is possible in an investigation but perhaps not in an industrial scale quality control and amorphous content impact both the CEC and the chemical content, hence it is observed elsewhere. There are more advanced and mild ways to mill the clay, e.g. by wet milling in alcohol, and to prepare a more randomly oriented sample by spray drying, beneficial for the XRD evaluation. This was however not regarded as suitable alternatives in a non-research laboratory.

Additional investigation of the coarse fraction with XRD and μ-RAMAN spectroscopy give complementary information and this is expected to increase the quality of the XRD evaluation in the future. Hence, there are even more delicate ways to find differences between or within the batches, but the aim in this case was to use methods that are optimised for industrial scale control and to see how well they could be used in this case.

By quantifying the other components in the clay fractions, a better value of the CEC of the montmorillonite could be calculated, and the method should then most likely give a montmorillonite content closer to the XRD method. This was not done in this work, however in the future a combination of infrared spectroscopy (FT IR) and XRD are expected to be useful for this.

Chemical data from XRF may be collected much more rapidly and with more ease compared to the other methods. With knowledge of the material, the chemical data may be used as an indirect montmorillonite indicator, however the method cannot be used on its own to determine montmorillonite or mineralogy. In the case of MX80, the Mg+Al/Si ratio worked well, while in the Milos bentonite it did not, as Mg was present in both montmorillonite and in the accessory minerals such as dolomite. Instead, in the Milos bentonites the Al/(Si+Fe) ratio fitted better with the results, however still not very good as such different bentonites were used. Further complementary information is then of value such as the exchangeable cations (EC) as they contribute to the chemical content. But more importantly, for a single type of bentonite within a batch, this kind of correlations is expected to work much better, especially if more data input is used, and if needed more complex calculations can be done easily.

Based on XRD, CEC, and XRF data (Table 19-4) is seems reasonable to say that the montmorillonite content was lowest in the MX-80 from 1993 and highest in the 2012 batch. The other MX-80 batches were somewhere in the middle of these batches (2002, 2006, 2015).

The difference between the Milos backfill clays is too small in relation to the scattering of data observed, due to the inhomogeneity of this material a better sample preparation is most likely needed to go into further details regarding differences in montmorillonite content in these two. The Ibeco 2011 was also investigated by Sandén et al. (2014). The Si content reported was somewhat lower and 64 wt% montmorillonite was reported from XRD measurements, compared to 59 % in this work. The Ibeco BF clays have a higher proportion of accessory minerals compared to MX80 and careful sampling to get a representative sample then becomes much more important, something that was not in focus in this study but needs to be taken much more into account in the real case situation.

The combination of XRD, CEC, XRF and EC is considered to be very powerful and useful for large scale quality control of the chemistry and mineralogy of bentonite batches in the future. Various complementary techniques such as IR and RAMAN spectroscopy, electron microscopy, thermogravimetrical (TGA) and differential thermal analysis (DTA) are expected to be needed sporadically to support the standard analysis. Especially for qualitative mineral identification which is an input for correct XRD quantification. Some of them may be available in house while others are preferably available at external laboratories (e.g. electron microscopy). Also, wet chemical methods such as determination of extractable Fe, Si and Al (CBD-method) and determination of Fe(II)/Fe(III) would contribute to the overall interpretation and is expected to be used as a complement.

The included methods were comparable to each other and to earlier reported results. One should remember that the exact level of the values in these methods is not of utmost importance, but a high reproducibility is, so that the methods can detect any inhomogeneity in the batches that may impact the performance.

XRD and XRF was able to detect a contamination in the range of 1–5 wt%. It remains to further evaluate how sensitive also CEC is to quantify the variations in the bentonite, and the impact from the variation of montmorillonite on the important properties such as swelling pressure and hydraulic conductivity in relation to their allowed intervals.

The combination of XRF and XRD is estimated to be able to detect contaminations as low as 0.5–5 wt% depending on the type of contamination (0.5 % for something totally different such as copper ore, sea salt etc; 5 % for something rather similar such as kaolin clay. Contamination by another bentonite may be totally undetected, but the properties are not expected to be affected by that kind of contamination.

# 21 Status of validation of the CEC method

Method validation is the process used to confirm that the analytical procedure employed for a specific test is suitable for its intended use. Results from method validation can be used to judge the quality, reliability and consistency of analytical results. A validation of Cu-tri method is extensive and there are still some questions to answer and work to be done. Different validation tests of the Cu-tri method have been performed, e.g. the linearity of calibration, limit of detection and quantification, but these tests are not discussed in this report because they are instrument specific. Unfortunately, no certified reference materials have been available for method validation. Instead bentonites of matrices MX80, Ibeco and Asha have been used for validation tests. Bulk sample of each matrix has been milled prior to analyse, using a planetary ball mill (Retsch PM400) with grinding jars of zirconium oxide, see Section 7.2.

Repeatability and within-laboratory reproducibility standard deviation are two parameters that specify the precision of the method, which both contribute to the overall measurement uncertainty of the method and this is evaluated in 21.1. As the cation exchange reaction is an equilibrium reaction, the relation between added Cu-tri complex and the mass of montmorillonite will influence the equilibrium, this is evaluated in 21.2. It is known that the edge sites of the montmorillonite (silanol and aluminol groups etc) may be deprotonated at higher pH and hence become negatively charged sites. The pH is also equivalent to the amount of $H^+$ in solution, and $H^+$ is a cation that also takes part in the cation exchange reactions. Hence, the effect of pH from the bentonite on the solution and on the CEC is evaluated in 21.3. Some samples are harder to disperse than others, especially clay fractions are hard to disperse after drying, and hence the effect from dispersion time is evaluated in 21.4. Short milling is expected to open up the available surface area of the montmorillonite, especially if cemented by another phase, while a long milling time is expected to possibly destroy the clay minerals and hence, decrease the CEC, this is evaluated in 21.5. The reaction time is expected to be very fast if purely diffusion controlled, but some sites may bind stronger than others, hence possibly introducing a kinetic effect on the exchange reaction, this is evaluated in 21.6.

## 21.1 Repeatability and within laboratory reproducibility

These milled bulk samples or reference samples have then been used for repeatability and within laboratory reproducibility tests of the Cu-tri method. CEC have been analysed with 15 repetitions on four different occasions ($n_{\text{total}} = 60$) with different performers and different batches of Cu tri-solutions (Figure 21-1 to Figure 21-3). Table 21-1 lists repeatability standard deviation and within laboratory reproducibility standard deviation of the Cu-tri method, having MX80, Ibeco and Asha bentonite as test material.

**Table 21-1. Repeatability and within laboratory reproducibility in the analysis of CEC with Cu-tri method.**

| Bentonite material (matrix) | Repeatability standard deviation % (n=15) | CEC mean cmol (+)/kg dry weight (n=60) | Within lab Reproducibility standard deviation % (n=60) |
|---|---|---|---|
| MX80 #14 2012<br>(sample id c65da6) | 2.1 | 85 | 2.1 |
| Ibeco backfill #18 2011<br>(sample id c65d8e) | 1.3 | 63 | 1.1 |
| Asha #179 2012<br>(sample id c65d8b) | 2.3 | 79 | 1.5 |

When analysing CEC with the Cu-tri method, data shows that repeatability and within laboratory reproducibility is within the expanded uncertainty (± 8 %) for all three matrices.

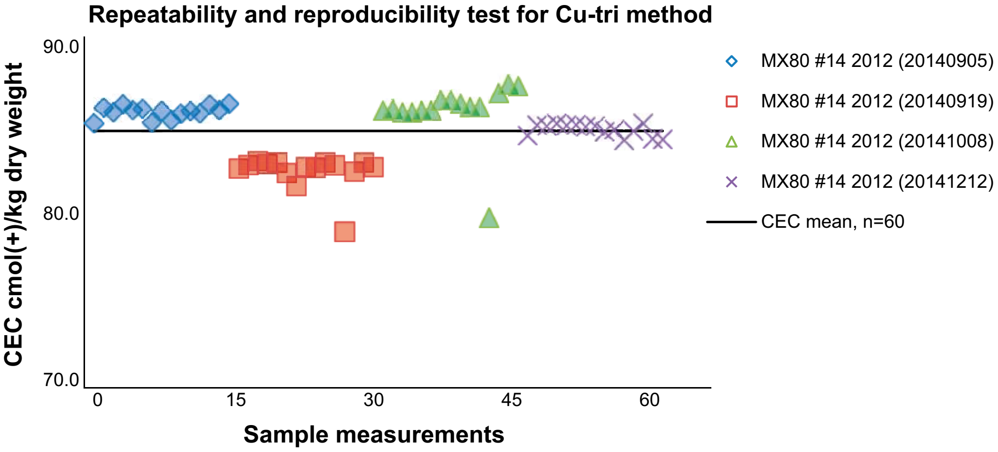

***Figure 21-1.*** *CEC data (n=60) for matrix MX80 #14 2012. Within laboratory reproducibility is estimated to about ± 2 % with the Cu-tri method.*

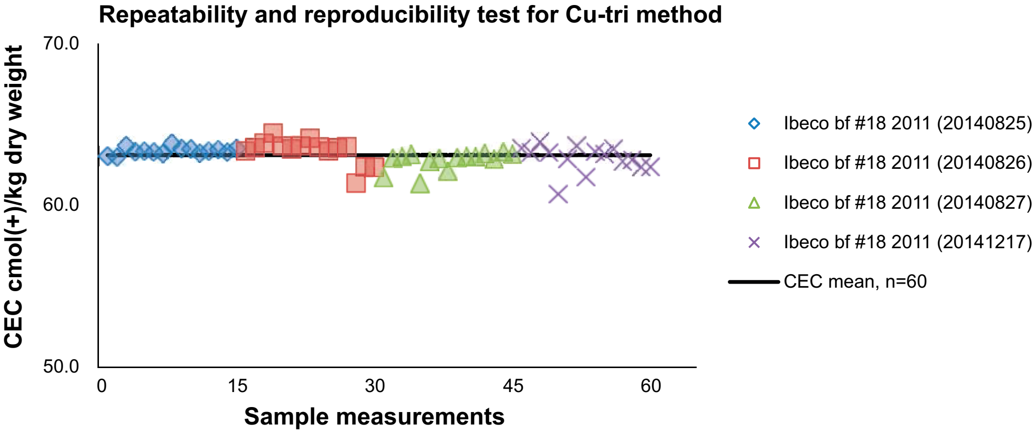

***Figure 21-2.*** *CEC data (n=60) for matrix Ibeco bf #18 2011. Within laboratory reproducibility is estimated to about ± 1 % with the Cu-tri method.*

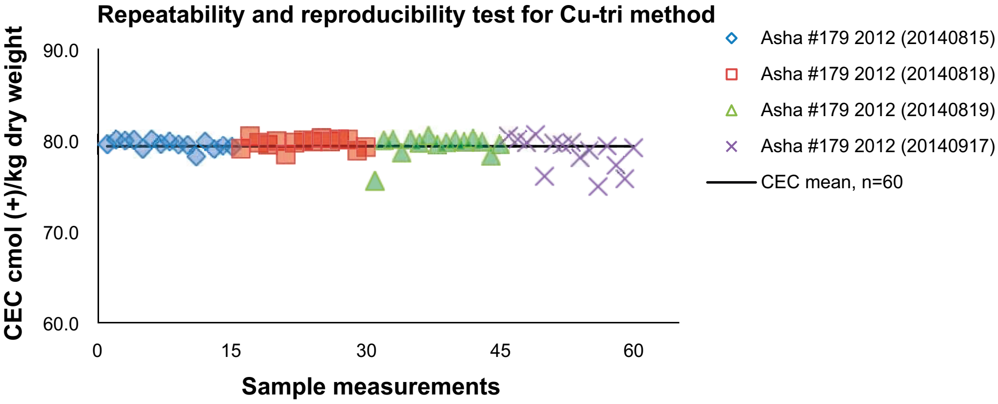

***Figure 21-3.*** *CEC data (n=60) for matrix Asha #179 2012. Within laboratory reproducibility is estimated to about ± 1.5 % with the Cu-tri method.*

## 21.2 Sample mass

CEC for samples of MX80, Asha and Ibeco matrices have been analysed and relative standard deviation (%RSD) of duplicates has been calculated. The dry weight of the samples varied from about 50 to 700 mg but same molar amount of $Cu^{2+}$ was added to the samples of each matrix. The reason was to see if the same CEC results were obtained despite different amounts (dry weight) of bentonite in the samples. In Table 21-2 to Table 21-4 the CEC results of these tests are listed. The tables also show the relative standard deviation (%RSD) of duplicates and the exchange of $Cu^{2+}$ for the different samples.

According to Cu-tri method the test amount of a sample is 400 mg (wet weight). Depending on the matrix the exchange of $Cu^{2+}$ (i.e. absorbed amount of $Cu^{2+}$ relative to the added amount of $Cu^{2+}$ to the clay) is about 40–60 % for samples with a wet weight of 400 mg.

When adding same molar amount of $Cu^{2+}$ it seems like the smaller amount of sample, the higher the CEC received (Figure 21-4 to Figure 21-6). However, relative standard deviation of duplicates is higher for smaller sample amounts, which contributes to a higher expanded measurement uncertainty (> 8 %) of the Cu-tri method.

At small sample masses, the concentration of Cu-tri in solution at equilibrium with the bentonite is higher (as the uptake was smaller), and hence, the equilibrium is expected to be forced further to form the Cu-tri montmorillonite, and hence the CEC somewhat increase. Possibly other effects also occur. As long as the measurement is done in an interval producing a stable CEC, the method is expected to work very well for quality control of bentonite.

**Table 21-2. Measured CEC as a function of sample mass (Wyoming/MX80 #14 2012).**

| Dry sample weight (g) | CEC (cmol(+)/kg dry weight) | %RSD (n=2) | Exchange $Cu^{2+}$ (%) |
|---|---|---|---|
| 0.05 | 106 | 4 | 8 |
| 0.09 | 96 | 2 | 14 |
| 0.18 | 90 | 3 | 27 |
| 0.37 | 86 | 1 | 51 |
| 0.73 | 79 | 1 | 92 |

The smallest sample amount (0.05 g) received the highest CEC-value (Figure 21-4). However, the smallest amount also showed a very low exchange of $Cu^{2+}$ and the largest %RSD of duplicates. A smaller amount of sample would thereby lead to a lower reproducibility of CEC and a larger expanded uncertainty (> 8 %) for the method.

**Table 21-3. Measured CEC as a function of the sample mass (Milos/Ibeco bf #18 2011).**

| Dry sample weight (g) | CEC cmol(+)/kg dry weight | %RSD (n=2) | Exchange $Cu^{2+}$ (%) |
|---|---|---|---|
| 0.05 | 93 | 14 | 7 |
| 0.09 | 71 | 7 | 11 |
| 0.18 | 72 | 1 | 21 |
| 0.37 | 70 | 1 | 42 |
| 0.73 | 65 | < 0.5 | 77 |

The smallest sample amount (0.05 g) received the highest CEC-value (Figure 21-5). However, the smallest amount also showed a very low exchange of $Cu^{2+}$ and the largest %RSD of duplicates.

**Table 21-4. Measured CEC as a function of the sample mass (Kutch/Asha #179 2012).**

| Dry sample weight (g) | CEC cmol(+)/kg dry weight | %RSD (n=2) | Exchange Cu2+ (%) |
|---|---|---|---|
| 0.05 | 122 | 2 | 9 |
| 0.09 | 102 | 3 | 15 |
| 0.18 | 94 | 2 | 27 |
| 0.36 | 87 | 2 | 50 |
| 0.72 | 78 | 1 | 89 |

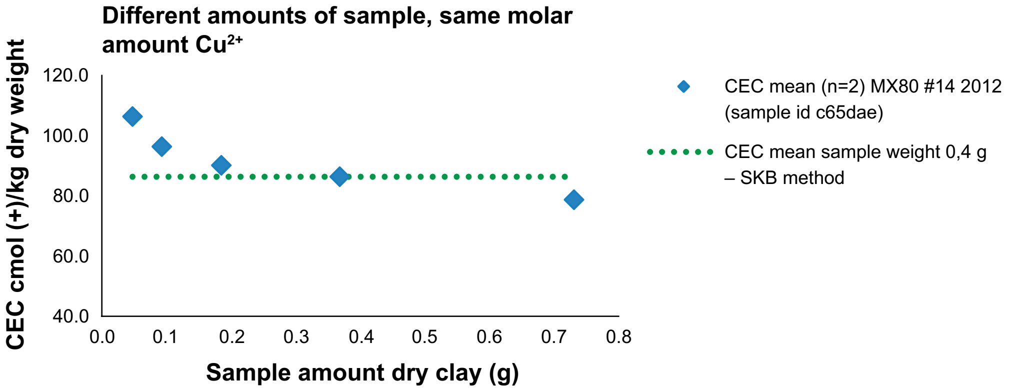

***Figure 21-4.*** *Measured CEC as a function of the sample mass (Wyoming/MX80#14 2012).*

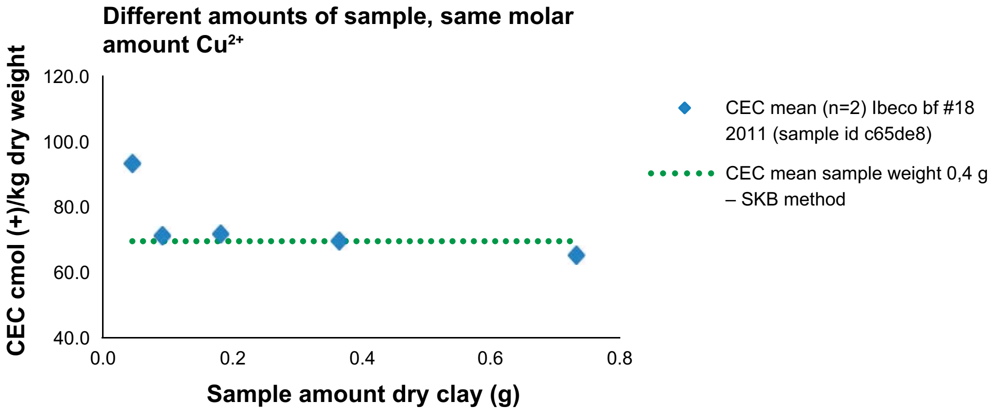

***Figure 21-5.*** *Measured CEC as a function of the sample mass (Milos/Ibeco bf #18 2011).*

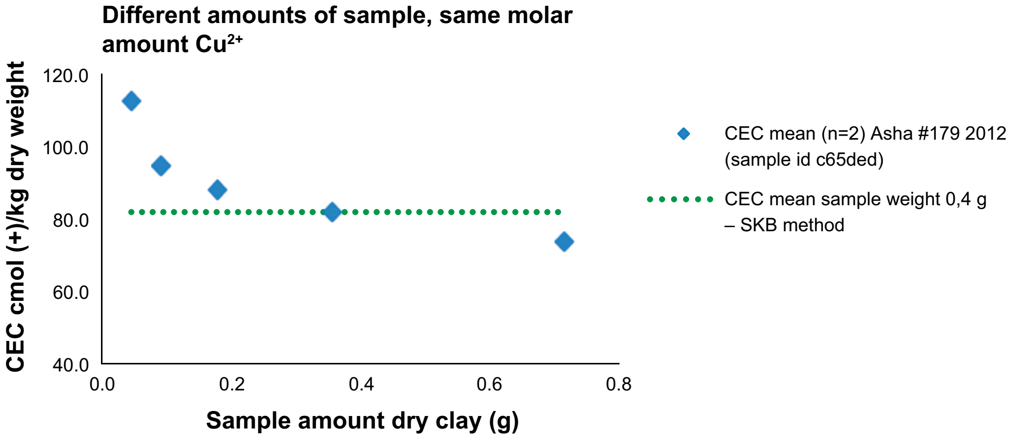

***Figure 21-6.*** *Same molar amount Cu2+ added to different sample amounts of Asha #179 2012. The smallest sample amount (0.05 g) received the highest CEC-value. However, the smallest amount also showed a very low exchange of Cu2+ and the largest %RSD of duplicates.*

Additional validation tests with certified reference material should be performed, to see if same results are obtained and estimate complete exchange. With a certified reference material the laboratory bias of the Cu tri-method can also be estimated.

## 21.3 Sample pH

In these tests pH was analysed before and after adding Cu-tri solution to bentonite samples (samples of MX80, Ibeco and Asha with a dry weight between 0.05 and 0.7 g). The bentonites were dispersed in deionised water on a vibrating table 30 minutes and then ultrasonic treated for 30 minutes. After centrifugation the supernatant was collected and pH analysed. The pH of the different samples decreased after adding Cu-tri solution; see Figure 21-7 to Figure 21-9. As the Cu-tri stabilised the pH (buffered) no pH effects are expected to affect the measurement.

The pH was found to be lower after addition of Cu-tri compared to prior the addition. The sample mass had no effect on the resulting pH after the Cu-tri addition (Figure 21-7 to Figure 21-9).

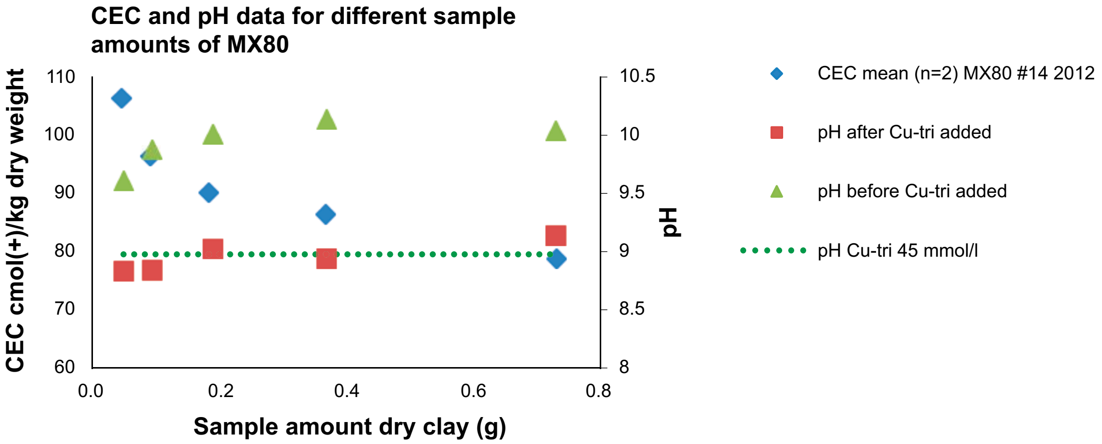

***Figure 21-7.** CEC and pH data for MX80.*

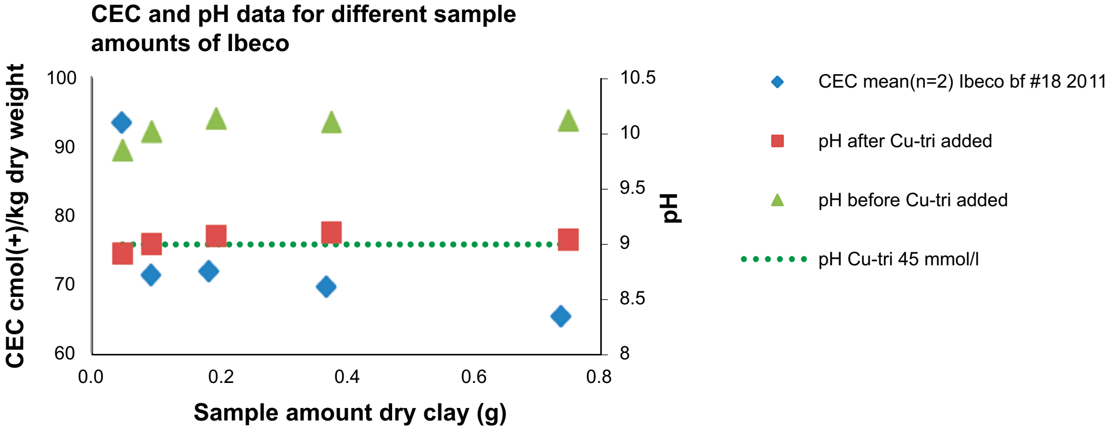

***Figure 21-8.** CEC and pH data for Ibeco.*

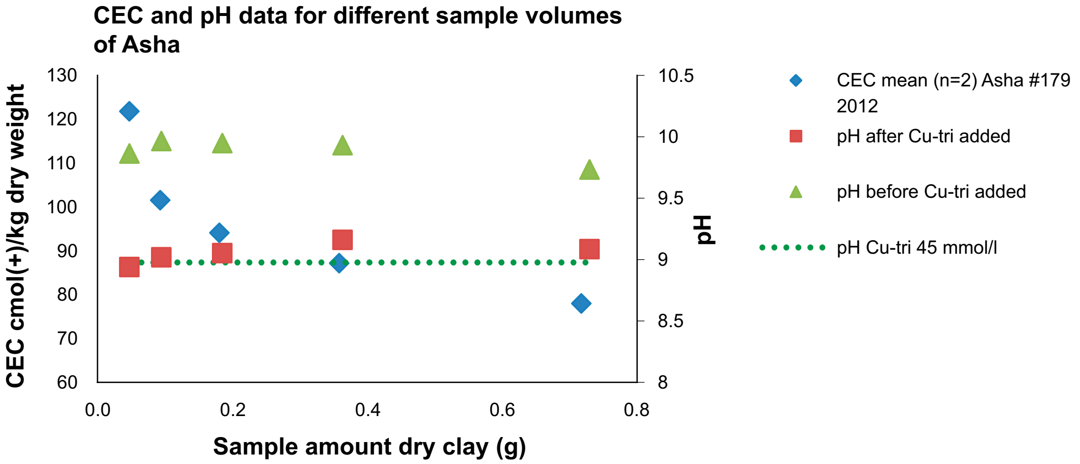

*Figure 21-9. CEC and pH data for Asha.*

## 21.4 Dispersion time

To see if the dispersion time of bentonite in deionised water has any effects on CEC, different samples of MX80, Ibeco and Asha bentonite were prepared. Duplicates of each sample were dispersed in filtered and deionised water; 1 min, 15 min, 30 min, 1 h, 2 h, 5 h, 3 days, 5 days and 61 days and then ultrasonic treated and analysed according to the Cu tri-method. In Figure 21-10 to Figure 21-12 CEC mean (n=2) are plotted for analysed samples with varied dispersion time. According to the Cu tri-method, samples should disperse 30 minutes in deionised water. Comparing CEC data for these samples it seems like the variation is within the expanded uncertainty for the method (U = ± 8 %). How long bentonite material should disperse in deionised water does not seem critical when considering minutes or hours.

No effect on the CEC was found on the dispersion time (Figure 21-10 to Figure 21-12).

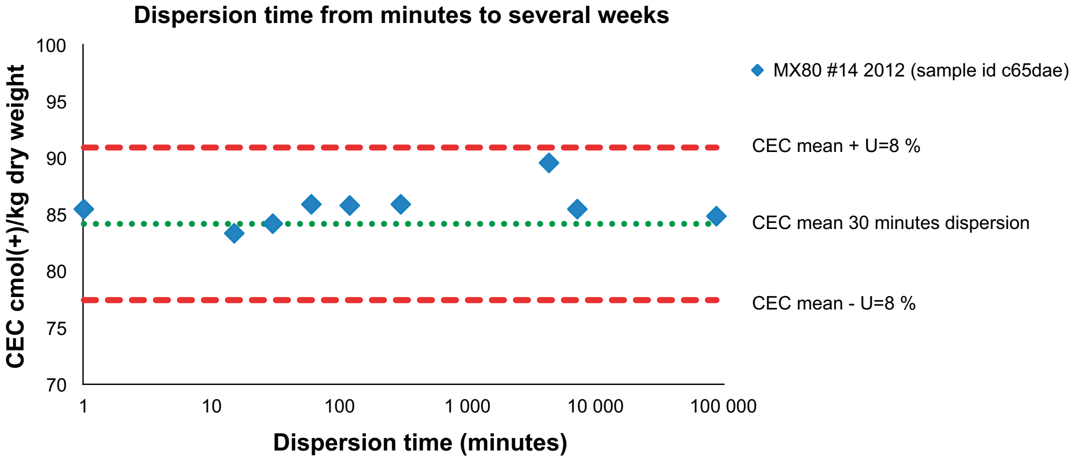

*Figure 21-10. Relative standard deviation of duplicates is beneath half expanded uncertainty (< 4 %) for all MX80 samples.*

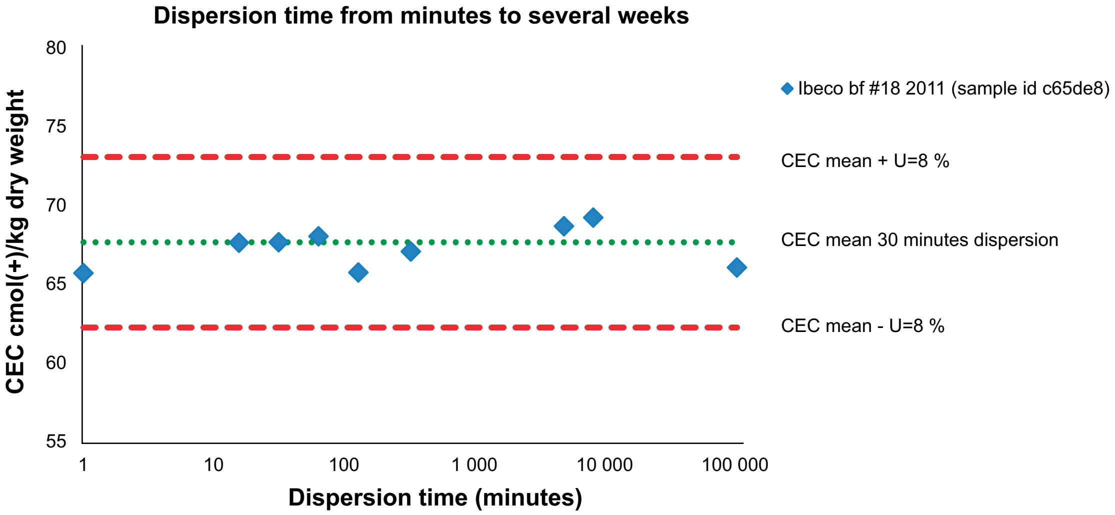

*Figure 21-11. Relative standard deviation of duplicates is beneath half expanded uncertainty (< 4 %) for all Ibeco samples.*

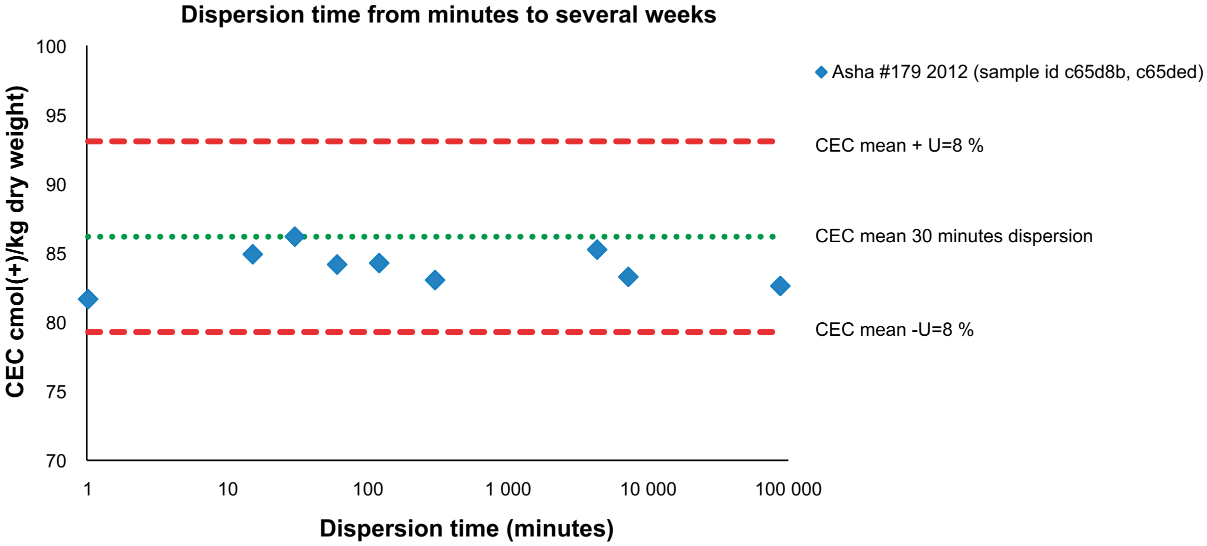

*Figure 21-12. Relative standard deviation of duplicates is beneath half expanded uncertainty (< 4 %) for all Asha samples.*

## 21.5 Reaction time

To see if the time which the bentonite reacts with $Cu^{2+}$ ions affects the CEC, different samples of MX80 were prepared. Duplicates of each sample were dispersed in deionised water 30 minutes and then ultrasonic treated 30 minutes. Cu-tri solution was then added and the samples were left on a vibrating table 1 min, 15 min, 30 min, 1 h, 2 h, 5 h, 6 days and 61 days before measured and quantified by spectrophotometry according to the SKB method. In Figure 21-13, CEC data for these duplicates are plotted. The data shows that the spread of CEC between duplicates (%RSD) is beneath half of the expanded uncertainty (< 4 %) for all samples. Although it seems like the CEC may slightly increase when the bentonite reacts a longer time with the Cu-tri solution. Samples with a reaction time of 61 days with Cu-tri solution show a CEC value 8 % higher compared to samples with a reaction time of 30 minutes. More tests could be carried out to verify if this is true or if it is an artefact, but it is not critical for the application if the time is fixed to 30 minutes or similar. The 30 minutes was selected for the method as it is a practical time, and a small variation in time ± 10 minutes, is not expected to impact the CEC.

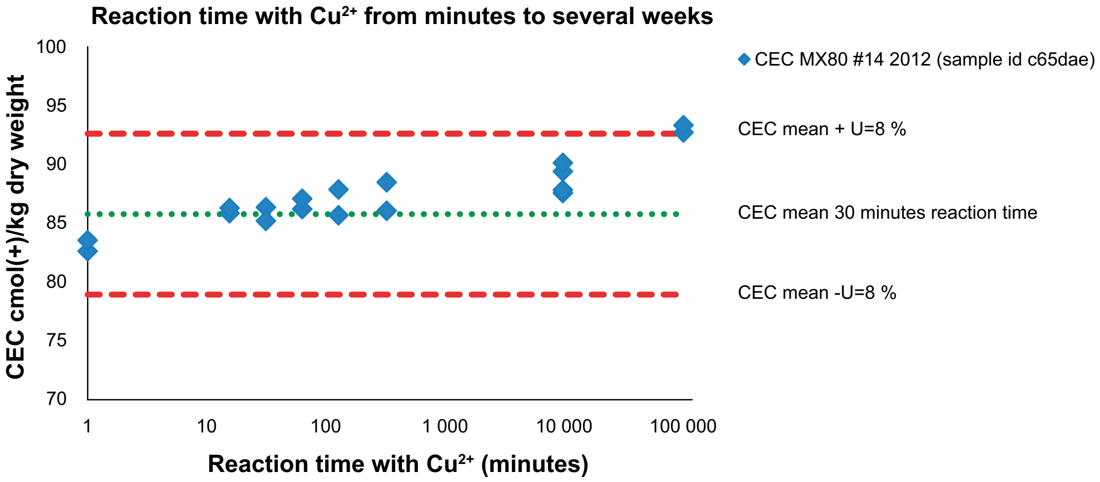

***Figure 21-13.*** *CEC as a function of reaction time (MX80 2012).*

The CEC seem to increase with increasing reaction time, however, very long reaction time may also possibly introduce various artefacts. It is however, important to use a single reaction time to get repeatable results (Figure 21-13).

## 21.6 Milling time

Milling seems to play a role for the CEC, however the different materials seems to respond differently and the effect is unclear. It is difficult based on these data to further analyse this, but to use the same milling time seems to be important to get repeatable results.

**Table 21-5. CEC after different milling times of the MX80 2012 bentonite.**

| Bentonite material (matrix) | CEC mean cmol(+)/kg dry weight (n=2) | %RSD (n=2) |
|---|---|---|
| MX80 #14 2012 bulk material (sample id c65d46) | 88 | 2 |
| MX80 #14 2012 bulk material milled 5 minutes (sample id c65dfc) | 94 | 2 |
| MX80 #14 2012 bulk material milled 10 minutes (sample id c65dfd) | 87 | 3 |
| MX80 #14 2012 bulk material milled 30 minutes (sample id c65dfe) | 83 | 5 |

**Table 21-6. CEC after different milling times of the Ibeco 2011 bentonite.**

| Bentonite material (matrix) | CEC mean cmol(+)/kg dry weight (n=2) | %RSD (n=2) |
|---|---|---|
| Ibeco bf #18 2011 bulk material (sample id c65d4f) | 64 | 1 |
| Ibeco bf#18 2011 bulk material milled 5 minutes (sample id c65df9) | 72 | 1 |
| Ibeco bf#18 2011 bulk material milled 10 minutes (sample id c65dfa) | 69 | 1 |
| Ibeco bf#18 2011 bulk material milled 30 minutes (sample id c65dfb) | 74 | 2 |

**Table 21-7. CEC after different milling times of the Asha 2012 bentonite.**

| Bentonite material (matrix) | CEC mean cmol(+)/kg dry weight (n=2) | %RSD (n=2) |
|---|---|---|
| Asha #179 2012 bulk material (sample id c65d67) | 85 | 7 |
| Asha #179 2012 bulk material milled 5 minutes (sample id c65dff) | 87 | 6 |
| Asha #179 2012 bulk material milled 10 minutes (sample id c65e00) | 88 | 5 |
| Asha#179 2012 bulk material milled 30 minutes (sample id c65e01) | 86 | 3 |

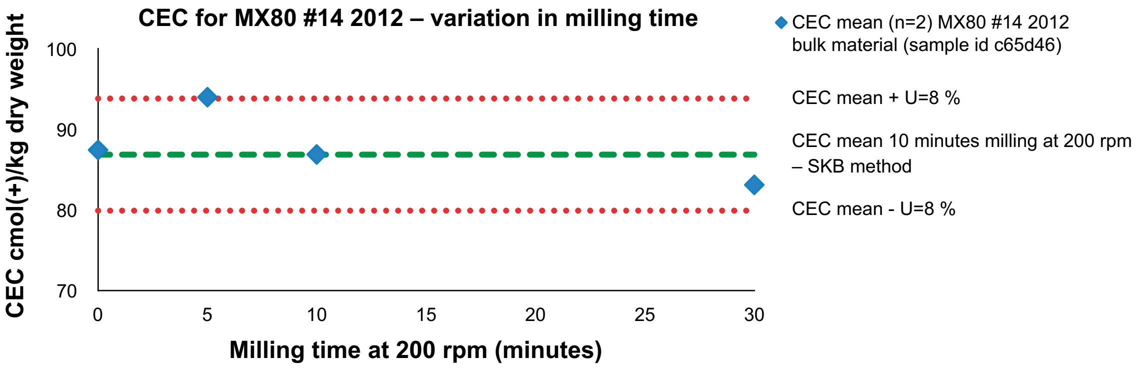

*Figure 21-14. CEC after different milling times of the MX80 2012 bentonite.*

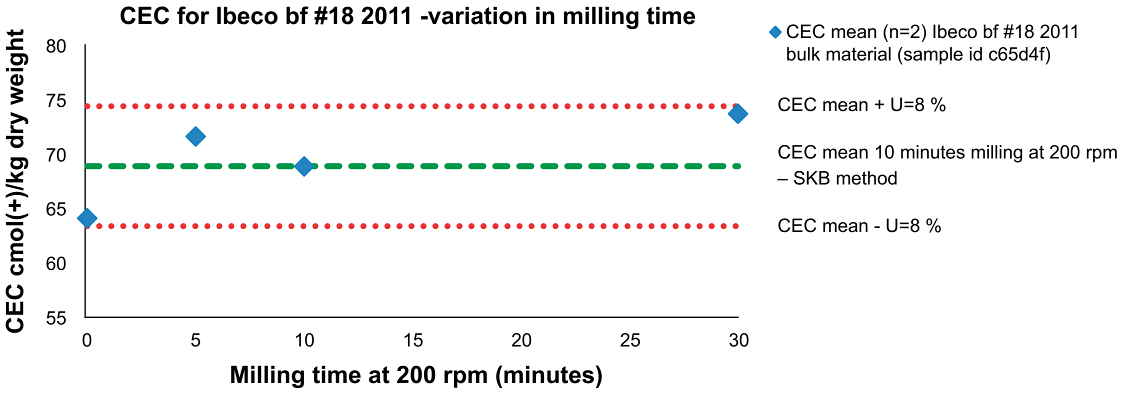

*Figure 21-15. CEC after different milling times of the Ibeco 2011 bentonite.*

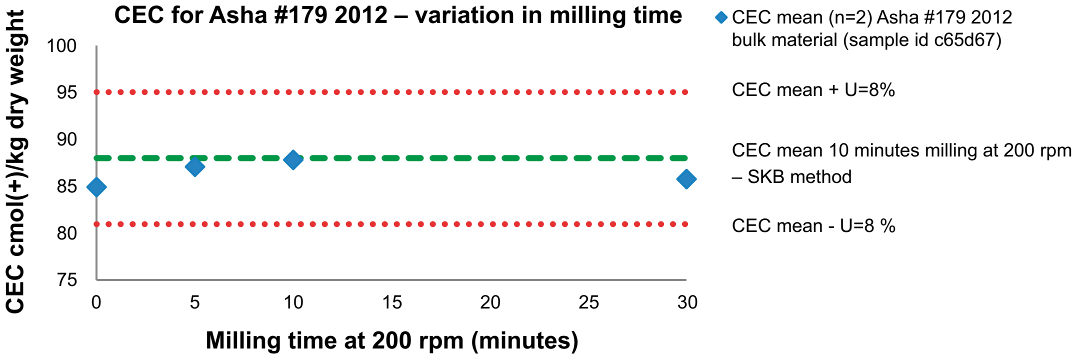

*Figure 21-16. CEC after different milling times of the Asha 2012 bentonite.*

## 21.7 Summary of CEC validation work

The repeatability of the method was very good with a reproducibility of around 2 %. The sample mass was found to be important for the measured CEC. For the mass used in the method description this is not a problem, however, it is important that the sample mass is relatively constant in order to get reproducible results. The pH was found to be lower after the Cu-tri addition compared to before. The amount of sample had no effect on the pH of the Cu-tri solution. The dispersion time did not show any significant effect on the CEC. The reaction time showed a clear trend that longer reaction increased the CEC, indicating that some exchangeable cations may take some time to replace, or possibly an artefact is causing the result. It is however important that the reaction time is constant in order to get high reproducibility of the method.

# 22 Conclusions

The following conclusions can be drawn from the performed work:

- A material laboratory for bentonite analysis was successfully developed as planned at Äspö. This research laboratory is expected to play an important role in the future of bentonite investigations at SKB.
- The laboratory methods used for determining the parameters affecting the technical requirements on the bentonite, such as swelling pressure, hydraulic conductivity and shear strength are described in detail. The methods have been tested and evaluated with good results.
- Some laboratory test which are used for describing the bentonite i.e. water content, bulk density, granule size distribution and compaction properties but are not related to any technical requirements are also described in detail.
- The complementary use of X-ray diffraction (mineralogy), X-ray fluorescence (chemistry) and Cation Exchange Capacity for characterisation was illustrated on a selection of Wyoming and Milos bentonite batches as delivered, and in the case of Wyoming also as when blended with sand, to simulate different buffer qualities and variations in the composition due to inhomogeneity of the delivery or due to contamination. It was found that an addition of 1 wt% of sand is around the limit of what is possible to detect with the current methods and a 5 % contamination is easily detected using XRF or XRD.
- XRF was found to be a fast and reliable method with high repeatability and is a recommended method for investigating variations (inhomogeneity) within bentonite batches, e.g. variations between bags.
- Montmorillonite content as determined from XRD was compared to as determined from CEC, overall it was a fairly good agreement, but it seemed that the montmorillonite chemistry and CEC changed somewhat between the different shipments during the approximately 20 years span between the first and last one, introducing differences. Hence, when correlating bentonite properties to montmorillonite content, it is expected to be better to use a single batch of bentonite and dilute with milled sand to simulate different qualities instead of comparing different batches with minor differences in montmorillonite content to exclude effects from variations in the clay mineral itself.
- For some of the investigated methods (e.g. XRD, XRF, CEC and EC) a milled bentonite material is recommended because it contributes to a more homogenous and more representative sample. It is important to keep in mind that long milling of bentonite material may affect the clay mineral properties. For other methods such as swelling pressure and hydraulic conductivity this is however not recommended as it may change the clay mineral properties.
- A validation process was initiated for the cation exchange capacity method, and a number of tests were performed and are included in the report in order to illustrate the complexity of bentonite analysis; and although the method works very well, there are still several factors that are less well understood. Validation tests of the CEC shows that the method has a high repeatability and within laboratory reproducibility standard deviation (2 %) for investigated matrices. The sample mass had a clear effect on the measured CEC, but the effect was very small in the vicinity of the mass selected in the method. The Cu-tri solution buffered the pH and hence after the addition the type and amount of bentonite did not affect the pH of the solution. The dispersion time had no significant effect on the measured CEC, however, the reaction time had a clear impact, but the interval 10–100 minutes was very stable, which is suitable for laboratory conditions. In some cases the CEC was affected by milling of the bentonite, but the results were inconclusive.
- The uncertainties of the methods need to be better quantified and compared to what is accepted. The current performance is expected by the authors to be good enough, but it remains to be shown by evaluating the impact of small amounts of contaminations on the important properties of the bentonite in relation to what can be detected.

# References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.com/publications.

**Ammann L, Bergaya F, Lagaly G, 2005.** Determination of the cation exchange capacity of clays with copper complexes revisited. Clay Minerals 40, 441–453.

**Arthur, R., Apted, M., Stenhouse, M., 2005.** Comment on the long-term chemical and mineralogical stability of the buffer. *Swedish Nuclear Power Inspectorate*, SKI Report 2005:9.

**Arvidsson A, Josefsson P, Eriksson P, Sandén T, Ojala M, 2015.** System design of backfill. Project results. SKB TR-14-20, Svensk Kärnbränslehantering AB.

**ASTM D5334-14.** Standard test method for determination of thermal conductivity of soil and soft rock by thermal needle probe procedure. West Conshohocken, PA: ASTM International.

**Atkins P W, 1998.** Physical chemistry. Student's solutions manual for Physical chemistry. 6th ed. Oxford: Oxford University Press.

**Bergaya F, Theng B K G, Lagaly G (eds), 2006.** Handbook of clay science. Developments in clay science. Volume 1. Amsterdam: Elsevier Science.

**Belyayeva N I, 1967.** Rapid method for the simultaneous determination of the exchange capacity and content of the exchange capacity and content of exchangeable cations in solonetzic soils. Soviet Soil Science 1409–1413.

**Birgersson M, Karnland O, Nilsson U, 2008.** Freezing in saturated bentonite – A thermodynamic approach. Physics and Chemistry of the Earth, Parts A/B/C 33, S527–S530.

**Brindley G W, Brown G, 1980.** Crystal structures of clay minerals and their x-ray identification. London: Mineralogical Society. (Mineralogical Society Monograph 5)

**Börgesson L, Hökmark H, Karnland O, 1988.** Rheological properties of sodium smectite clay. SKB TR 88-30, Svensk Kärnbränslehantering AB.

**Börgesson L, Fredriksson A, Johannesson L-E, 1994.** Heat conductivity of buffer materials. SKB TR 94-29, Svensk Kärnbränslehantering AB.

**Dueck A, Börgesson L, Johannesson L-E, 2010.** Stress-strain relation of bentonite at undrained shear. Laboratory tests to investigate the influence of material composition and test technique. SKB TR-10-32, Svensk Kärnbränslehantering AB.

**ISO 10725:2000.** Acceptance sampling plans and procedures for the inspection of bulk materials. Geneva: International Organization for Standardization.

**ISO 11648-1:2003.** Statistical aspects of sampling from bulk materials. Geneva: International Organization for Standardization.

**Jackson M L, 1975.** Soil chemical analysis: advanced course. 2nd ed. Madison, WI: University of Wisconsin.

**Johannesson L-E, 2014.** KBS-3H. Manufacturing of buffer and filling components for the Multi Purpose Test. SKB P-14-07, Svensk Kärnbränslehantering AB.

**Karnland O, 2010.** Chemical and mineralogical characterization of the bentonite buffer for the acceptance control procedure in a KBS-3 repository. SKB TR-10-60, Svensk Kärnbränslehantering AB.

**Karnland O, Muurinen A, Karlsson F, 2005.** Bentonite swelling pressure in NaCl solutions – Experimentally determined data and model calculations. In Alonso E E, Ledesma A (eds). Advances in understanding engineered clay barriers. Leiden: A. A. Balkema, 241–256.

**Karnland O, Olsson S, Nilsson U, 2006.** Mineralogy and sealing properties of various bentonites and smectite-rich clay materials. SKB TR-06-30, Svensk Kärnbränslehantering AB.

**Klein C, Hurlbut C S, 1998.** Manual of mineralogy. 21st ed. New York: Wiley.

**Kodama H, 1966.** The nature of the component layers in rectorite. American Mineralogist 51, 1035–1055.

**Komine H, Ogata N, 2004.** Predicting swelling characteristics of bentonites. Journal of Geotechnical and Geoenvironmental Engineering 130, 818–829.

**Laird D A, 2006.** Influence of layer charge on swelling of smectites. Applied Clay Science 34, 74–87.

**Meier L P, Kahr G, 1999.** Determination of the cation exchange capacity (CEC) of clay minerals using the complexes of copper(II) ion with triethylenetetramine and tetraethylenepentamine. Clays and Clay Minerals 47, 386–388.

**Moore D M, Reynolds R C, 1997.** X-ray diffraction and the identification and analysis of clay minerals. 2nd ed. Oxford: Oxford University Press.

**Newman A C D (ed), 1987.** Chemistry of clays and clay minerals. Harlow: Longman. (Mineralogical Society Monograph 6)

**Norrish K, 1954.** The swelling of montmorillonite. Discussions of the Faraday Society 18, 120–134.

**Patterson A L, 1939.** The Scherrer formula for x-ray particle size determination. Physical Review 56, 978–982.

**Posiva SKB, 2017.** Safety functions, performance targets and technical design requirements for a KBS-3V repository. Conclusions and recommendations from a joint SKB and Posiva working group. Posiva SKB Report 01, Posiva Oy, Svensk Kärnbränslehantering AB.

**Roskill, 2008.** The economics of bentonite. 11th ed. Roskill Market Report.

**Sandén T, Olsson S, Andersson L, Dueck A, Jensen V, Hansen E, Johnsson A, 2014.** System design of backfill. Investigation of backfill candidate materials. SKB R-13-08, Svensk Kärnbränslehantering AB.

**Sandén T, Andersson L, Jensen V, 2015.** System design of backfill. Full scale production test of backfill blocks. SKB P-14-24, Svensk Kärnbränslehantering AB.

**Segad M, Jönsson B, Åkesson T, Cabane B, 2010.** Ca/Na montmorillonite: structure, forces and swelling properties. Langmuir 26, 5782–5790.

**Segad M, Jönsson B, Cabane B, 2012.** Tactoid formation in montmorillonite. The Journal of Physical Chemistry C 116, 25425–25433.

**SIS-CEN ISO/TS 17892-1:2005.** Geotechnical investigation and testing – Laboratory testing soil. Part 1: Determination of water content. Stockholm: Swedish Standards Institute.

**SIS-CEN ISO/TS 17892-1:2005.** Geotechnical investigation and testing – Laboratory testing of soil – Part 2: Determination of density of fine-grained soil. Stockholm: Swedish Standards Institute.

**SIS-CEN ISO/TS 17892-4:2013.** Geotechnical investigation and testing – Laboratory testing of soil – Part 4: Determination of particle size distribution. Stockholm: Swedish Standards Institute.

**Svensson D, Dueck A, Nilsson U, Olsson S, Sandén T, Lydmark S, Jägerwall S, Pedersen K, 2011.** Alternative buffer material. Status of the ongoing laboratory investigation of reference materials and test package 1. SKB TR-11-06, Svensk Kärnbränslehantering AB.

**Svensson P D, 2015.** The bentonite barrier: swelling properties, redox chemistry and mineral evolution. PhD thesis. Lund University.

**Svensson P D, Hansen S, 2010.** Freezing and thawing of montmorillonite – A time-resolved synchrotron X-ray diffraction study. Applied Clay Science 49, 127–134.

**Svensson P D, Hansen S, 2013.** Combined salt and temperature impact on montmorillonite hydration. Clays and Clay Minerals 61, 328–341.

**Stucki J W, Lee K, Zhang L, Larson R A, 2002.** Effects of iron oxidation state on the surface and structural properties of smectites. Pure and Applied Chemistry 74, 2145–2158.

**UNCTAD, 2013.** Review of maritime transport 2013. Available at: http://unctad.org/en/PublicationsLibrary/rmt2013_en.pdf

**VanLoon Gary W, Duffy Stephen J, 2000.** Environmental Chemistry – A global perspective. Oxford: Oxford University Press.

**Örnemark U, 2001.** Methodology I, Utvärdering av mätosäkerhet i kemisk analys. 2nd ed. SP rapport 2001:24, Sveriges provnings- och forskningsinstitut. (In Swedish.)

Arkitektkopia AB, Bromma, 2018

SKB is responsible for managing spent nuclear fuel and radioactive waste produced by the Swedish nuclear power plants such that man and the environment are protected in the near and distant future.

**skb.se**

SVENSK KÄRNBRÄNSLEHANTERING