

# Technical Report

## TR-10-60

### **Chemical and mineralogical characterization of the bentonite buffer for the acceptance control procedure in a KBS-3 repository**

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September 2010

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## Abstract

The present report concerns the chemical and mineralogical characterization of potential buffer materials. A short mineralogical description of bentonite and montmorillonite is given. The report defines, and exemplifies analyses and tests planned for the acceptance control of the bulk material concerning chemical composition, mineralogical composition, original exchangeable cations, cation exchange capacity (CEC), grain density, specific surface area, granule size, water content. In addition, analyses of the clay fraction, i.e. material with a grain size smaller than 2  $\mu\text{m}$ , are described with respect to chemical composition including layer charge, layer charge distribution and cation exchange capacity (CEC). Results from the report by /Karnland et al. 2006/ concerning the two reference bentonites MX-80 and IBECO RWC are used to illustrate the accuracy and precision of the analyses.

For each type of analyses the purpose, technique and, in relevant cases, also limits are discussed briefly. An empirical model for determining swelling pressure is presented and used for the quantification of the expected sealing properties given the limits concerning buffer density and montmorillonite content. For the reference bentonites MX-80, the stipulated montmorillonite content interval from 0.75 to 0.9 gives a pressure interval from 8 to 11 MPa at the nominal saturated density 2,000  $\text{kg/m}^3$ . The stipulated saturated density interval from 1,950 to 2,050  $\text{kg/m}^3$  gives a pressure range from 6 to 15 MPa at the measured montmorillonite content of 83% by weight. The combined effects of the stipulated montmorillonite content interval and saturated density interval lead to a pressure range from 5 to 17 MPa. If the increasing effect of accessory minerals, which is proposed by the model, is not taken into account then the combined pressure range is 3 to 14 MPa.

## Sammanfattning

Rapporten berör kemisk och mineralogisk karakterisering av tänkbara buffertmaterial. En kort mineralogisk beskrivning av bentonit och montmorillonite ges, samt definitioner och exempel på de tester som är tänkta att ingå i en mottagningskontroll av bulkmaterial. För närvarande avser detta kemisk komposition, mineralogiskt komposition, ursprungliga utbytbara katjoner, katjonbyteskapacitet (CEC), korndensitet, specifik area, kornstorlek och vattenkvot. Vidare beskrivs analyser av lerfraktionen, dvs material med en kornstorlek mindre än  $2\mu\text{m}$ , med avseende på kemisk komposition, ur vilken också flakladdningen, laddningens fördelning och jonbyteskapacitet (CEC) framgår. Resultat från /Karnland et al. 2006/ som berör de två referensbentoniterna MX-80 och IBECO RWC används för att illustrera precisionen och noggrannheten i de angivna analyserna.

Analyserna beskrivs kortfattat med avseende på motiv till analysen, metoden som används, samt i relevanta fall, också acceptansgränser. En empirisk modell för att bestämma svälltryck beskrivs och används för att kvantifiera de förväntade tätningsegenskaperna som följer av de angivna gränserna för densitet och montmorillonitnehåll. För referensbentoniten MX-80 beräknas svälltrycken bli mellan 8 och 11 MPa för det angivna montmorillonitintervallet 0.75 till 0.9 vid den nominella vattenmättade densiteten  $2\ 000\ \text{kg/m}^3$ . Det angivna densitetsintervallet mellan  $1\ 950$  och  $2\ 050\ \text{kg/m}^3$  beräknas ge ett tryckintervall på mellan 6 och 15 MPa vid den uppmätta montmorillonithalten på 83 viktsprocent. Den kombinerade effekten av de angivna gränserna för montmorillonitnehåll och densitet beräknas ge ett maximalt tryckintervall på mellan 5 och 17 MPa. Om den tryckhöjande effekten från accessoriska mineral, som modellen innehåller, inte beaktas är motsvarande intervall 3 till 14 MPa.

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# 1 Introduction

The central purpose of the bentonite buffer in the KBS-3 repository is to protect the copper canister. The most important functions are to limit transport of dissolved corroding agents to the copper canister and reduce bacterial activity in the vicinity of the copper canister. In order to accomplish these demands, the buffer has to mechanically hold the canister in position, reduce ground-water flow and exert a swelling pressure. At the same time, the buffer may not jeopardize the canister functions by chemical or mechanical interaction (see Section 3).

There are industry standards available that provide specifications for bentonite for specific purposes such as for drilling mud, foundries, cosmetics and pharmaceuticals /Eisenhour and Reisch 2006/. Such specifications are consequently developed with a particular application in mind and are not well suited for specifications of the bentonite in a repository. As an example, typical industry parameters may vary considerably depending on the type of charge compensating cations in the bentonite. In the bentonite buffer, these cations may change significantly over time, mainly depending on the chemical evolution of the surrounding groundwater. Specific favorable properties of a particular charge compensating cation can consequently not be taken into account, and the specification of the bentonite buffer has in principle to be based on the least favorable potential conditions over the whole lifetime of the repository. The specification of the bentonite buffer material has therefore to be based on basic and measurable parameters. The objectives with the following report are to describe and motivate the 1) chosen parameters, 2) the methods to determine parameter values, 3) the specific demands on the bentonite with respect to these parameters. The discussion and conclusions in the present report are largely based on the experimental results in the Technical Report TR-06-30 /Karnland et al. 2006/, in which relations between bentonite mineralogy and the physico-chemical properties of different bentonites are analyzed.

In SR-Site, a bentonite with a montmorillonite content of 80 to 85% has been selected as buffer reference material. As examples of such a reference material, the same two commercial bentonites MX-80 and IBECO RWC as were used in SR-Can are also used in SR-Site, since they are expected to meet the specifications in the reference design. The brand name MX-80 represents a western, or Wyoming, sodium dominated bentonite supplied by the American Colloid Company. Likewise, the brand name IBECO RWC (previously called Deponit Ca-N) represents a Greek calcium dominated bentonite supplied by Silver & Baryte Mining Company. Both these bentonites are mined in huge deposits by big bentonite suppliers. They are of different age, origin, have different dominant charge-compensating cations, and have different sets of accessory minerals, but may still be seen as relevant illustrations of possible alternatives for buffer material in a repository. The two bentonites are used in the following to illustrate the accuracy and precision of the analyzing methods and discussions concerning the defined limits. Some references are also made to a beidellitic bentonite from Ashapura Mining Company called Asha 229, and to the more extreme low grade Friedland ton material.

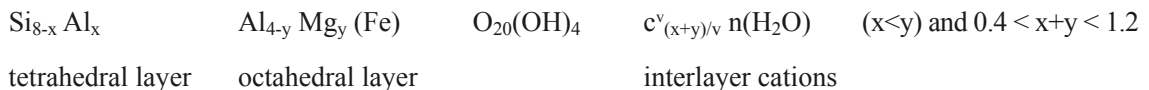
## 2 General bentonite mineralogy

Bentonite is a geological term for soil materials with a high content of a swelling mineral, which usually is montmorillonite. The remaining part of the bentonite may vary substantially in mineralogy within, and especially between different quarries, and depends basically on the geochemical conditions during the formation of the bentonite. Typical accessory minerals present in bentonites are other clay minerals, quartz, feldspars, gypsum, calcite, pyrite and various iron oxides/hydroxides. Also amorphous and organic compounds may be present in significant amounts.

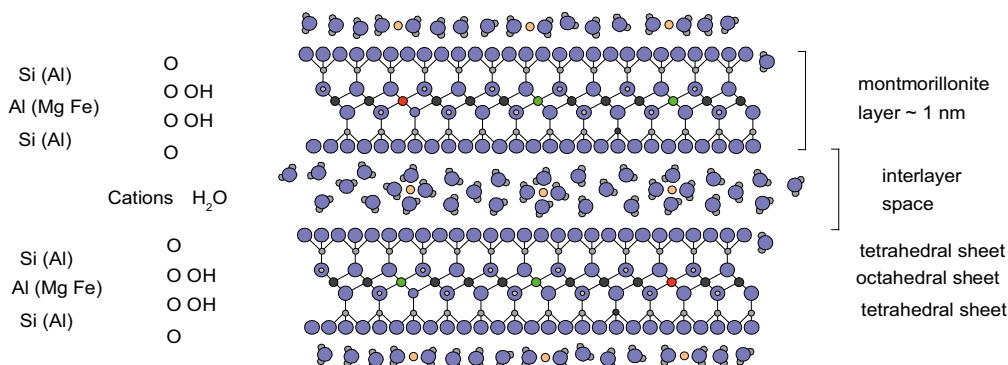
The montmorillonite mineral belongs to the smectite mineral group, in which all members have an articulated layer structure and swelling properties. Common for the smectite group is that the thickness of an individual mineral layer is around 1 nm and the extension of the other two directions may be up to several hundred nanometers. Each layer is composed of a central sheet of octahedrally coordinated cations, which on both sides are linked through shared oxygens to sheets of tetrahedrally coordinated cations. Minerals of this type are often referred to as 2:1 layer structures.

By definition, originally based on the physical properties of the minerals, the following applies for the mineral montmorillonite (see also Figure 2-1). The octahedral sheet has aluminum as central atom, which partly is substituted by principally magnesium. The surrounding tetrahedral sheets have silicon as central atom, which partly may be substituted principally by aluminum. The substitutions results in a net negative electrical charge of the montmorillonite layer in the range of 0.4 to 1.2 unit charges per  $O_{20}(OH)_4$  layer unit. In montmorillonite, the charge emanating from octahedral layer is higher than the charge emanating from the tetrahedral layer. The mineral is termed beidellite if the charge emanating from the tetrahedral layer is dominating. The negative layer charge is always balanced by cations (c) due to the fundamental demand in nature for electrical neutrality. The charge balancing cations are located between the individual layers (interlayer space). A variable number (n) of water molecules may be intercalated between the individual mineral layers, i.e. the distance between the individual layers increase by water uptake /Newman and Brown 1987/. The total volume of a clay containing montmorillonite will thereby increase macroscopically, which commonly is named swelling.

The montmorillonite ideal formula may accordingly be written:



Where v represents the mean valence of the charge compensating cations.



**Figure 2-1.** Edge view cartoon of two montmorillonite layers with interlayer cations and water molecules (perpendicular to the c-axis). Based on the mineral description in /Newman and Brown 1987, Brindley and Brown 1980/.

The charge balancing, or compensating, cations are principally bound by electrostatic forces, which make them exchangeable in a hydrated state. The frequently used terms “interlayer cations”, “exchangeable ions” and “charge compensating cations” do thus normally represent the same thing in montmorillonite. In natural bentonite, the charge balancing cations are rarely of one element alone, but a mixture of both mono and divalent ions. Several physico-chemical properties are to a large extent dependent on the type of the dominating charge balancing cation. The dominating cation is therefore often used to describe the type of bentonite, e.g. sodium bentonite.

There is a large variation in mineral composition within the smectite group, which has motivated specific mineral names, e.g. nontronite for an iron-rich variety, and saponite for a magnesium-rich type. Further, the smectite group includes minerals which have layer charges outside the charge limits of the montmorillonite, which give these minerals significantly reduced swelling properties. This has motivated other mineral names, e.g. vermiculite for charge above 1.2 unit charges per  $O_{20}(OH)_4$ -unit. Minerals with this high mean layer charge, and potassium as charge compensating ion, usually have some layers which do not separate at all in contact with water, i.e. these layers do not swell. Such a material mix of swelling and non-swelling layers is generally termed mixed layer smectite-illite. The share of non-swelling (illitic) layers increase with increasing mean layer charge, and at 2 unit charges per  $O_{20}(OH)_4$ -unit there is normally no swelling layers. Such a mineral belongs to the mica group and may in this case specifically be termed muscovite.



### 3 Specific demands on the bentonite buffer in KBS-3 repository

An important safety function of the buffer is to limit transport of dissolved copper corroding agents to the canister and potential radionuclide releases from the canister /SKB 2006/. The buffer material which surrounds the canister has been chosen so as to prevent advective transport in the deposition hole. A guideline is that the hydraulic conductivity of the buffer ( $k_{buffer}$ ) should fulfill:

$$k_{buffer} < 10^{-12} m/s \quad \text{Equation 3-1}$$

The requirement refers to all parts of the buffer, i.e. the variability within the buffer must be such that the requirement is everywhere fulfilled. For any reasonable hydraulic gradient in the repository, this condition will mean that transport in the buffer will be dominated by diffusion. The hydraulic conductivity is strongly related to the density of the buffer, to the adsorbed ionic species and to the ionic strength of the surrounding groundwater. The buffer homogeneity is ensured partially by the fact that the buffer is made of a clay material that swells when water saturated. A swelling pressure criterion is therefore formulated:

$$P_{swell}^{buffer} > 1 \text{ MPa} \quad \text{Equation 3-2}$$

The requirement refers to all parts of the buffer, i.e. the variability within the buffer must be such that the requirement is everywhere fulfilled.

The buffer should furthermore have a sufficient swelling pressure to prevent bacteria from being active in it. Past and ongoing studies indicate that this will occur at swelling pressures exceeding 2 MPa. This leads to the criterion:

$$P_{swell}^{buffer} > 2 \text{ MPa}, \text{ (eliminate microbial activity)} \quad \text{Equation 3-3}$$

The requirement refers to all parts of the buffer, i.e. the variability within the buffer must be such that the requirement is everywhere fulfilled /SKB 2006/.

## 4 Characterization of the bentonite buffer

### 4.1 General

In the SR-Can buffer process report /SKB 2006/ the chemical state of the buffer is defined by its mineralogy, including the montmorillonite composition, other clay minerals, and any other impurities. The chemical state is also defined by the porewater composition and the occurrence of structural and stray materials in the deposition hole. The variables are defined in Table 4-1.

In order to identify and validate the key variables for the chemical and sealing properties of a buffer material, the following characteristics of different bentonite materials were determined in /Karnland et al. 2006/. The results are here used to formulate the mineralogical part of the quality control program for a KBS-3 repository in order to achieve a reliable production. The outcomes from the included analyses will not be directly used for inspection of the design parameters for the initial state, but they will be used to ensure that the incoming material is acceptable and thereby reduce the variability of the produced buffer. The following characteristics for the bentonite bulk material are included.

- Chemical composition
- Mineralogical composition
- Original exchangeable cations
- Cation exchange capacity (CEC)
- Grain density
- Specific surface area
- Granule size
- Water content

**Table 4-1. Definition of buffer variables defined in the SR-Can buffer process report.**

| Variable                            | Definition  |
|-------------------------------------|---|
| Buffer geometry                     | Geometric dimensions for buffer. An example is description of interfaces (on the inside towards the canister and on the outside towards the geosphere).           |
| Pore geometry                       | Pore geometry in buffer as a function of time and space. The total porosity, (the fraction of the volume that is not occupied by solid material) is often given.  |
| Radiation intensity                 | Intensity of ( $\alpha$ , $\beta$ , $\gamma$ ) and neutron radiation as a function of time and space in buffer.   |
| Temperature                         | Temperature as a function of time and space in buffer.  |
| Water content                       | Water content as a function of time and space in buffer.  |
| Gas content                         | Gas content (including any radionuclides) as a function of time and space in buffer.  |
| Hydrovariables (pressure and flows) | Flows and pressures of water and gas as a function of time and space in buffer.   |
| Stress state                        | Stress conditions as a function of time and space in buffer.  |
| Bentonite composition               | Chemical composition of the bentonite (including any radionuclides) in time and space in buffer, levels of impurities in time and space in buffer.                |
| Montmorillonite composition         | The mean molecular structure of montmorillonite including the type of charge compensating cations   |
| Porewater composition               | Composition of the porewater (including any radionuclides and dissolved gases) in time and space in the buffer.   |
| Structural and stray materials      | Chemical composition and quantity of any stray materials accidentally left in the buffer. At this stage, no structural materials are defined for this component . |

In addition, the following characteristics of the clay fraction of the bentonite materials are included:

- Chemical composition
- Structural formula based on the chemical composition of the clay fraction
- Cation exchange capacity (CEC)

The structural formulas and the CEC values give independent quantifications of the layer charge of the clay mineral. The structural formulas also include the layer charge distribution between the octahedral and tetrahedral sheets.

## 4.2 Bentonite composition

### 4.2.1 Chemical composition of bulk material

The raw bentonite material for the buffer production will most certainly vary to some extent, both with respect to type and distribution of minerals, since it is a natural material. Further, the bentonite may contain organic and amorphous matter and even artifacts. A relatively fast and cost effective way to get an indication of such variations in mean composition is to perform chemical analyses of the delivered bulk material. The chemical composition of the bulk material will therefore be analyzed for major element. As examples of results from standard ICP/AES analyses, the chemical compositions of the reference bentonites MX-80 and IBECO RWC are shown in Table 4-2 together with Asha 229 and Friedland ton /Karnland et al. 2006/.

Organic material in the buffer is a general nuisance, since its long-term behavior is difficult to predict. Sulfate minerals, like gypsum and anhydrite, have a relatively high solubility which decreases with increasing temperature. This may lead to accumulation of sulfate minerals in the inner part of the buffer during the thermal phase. Potential loss of all sulfates from the buffer to the groundwater, in a long term perspective, will lead to a decrease in the buffer density and a decrease in swelling pressure as a consequence. Finally, sulfides may corrode the copper canister. Organic carbon and sulfur is consequently of special interest and specific analyses of these elements will therefore be made.

Table 4-3 shows results concerning total carbon, organic carbon and carbonate carbon in the reference bentonites MX-80 and IBECO RWC and also in the Asha 229 and Friedland ton bentonites. In addition carbon analyses from reference MX-80 material from the LOT A2 test are shown in Table 4-4. The content of organic carbon in the clay fractions indicates that the organic carbon is relatively insoluble, since large amount of water was used in the preparation of the clay fraction material. The analyses were made by use of a Leco multiphase carbon analyzer equipped with an IR-detector for CO<sub>2</sub>, which separates the organic and inorganic carbon content by stepped heating from 100°C to 1,000°C.

Table 4-5 shows results for total sulfur, sulfate and sulfide content and calculated maximum possible pyrite content in the reference bentonites MX-80 and IBECO RWC and also in the Asha 229 and Friedland ton bentonites. Total sulfur was determined by combustion at 1,200°C in a standard Leco furnace. The sulfate content was determined by analyses of a separate sample ignited to 800°C. The sulfide content was thereafter calculated as the difference between total S content and the sulfate S content.

The **Design Premises** in SR-Site states that the sulfide content should not exceed 0.5% of the total dry mass, and the total content of sulfur, including the sulfide, should not exceed 1% of the dry mass. The total organic carbon content should not exceed 1% of the dry mass.

No further quantitative criteria for impurities in the buffer are defined at present. Some further restrictions related to common sense has thought to be discussed, and possibly regulated. Consider for example a potential bentonite where the accessory minerals are dominated by sodium chloride. Although the salt may be considered harmless in itself, the mass loss when the salt is dissolved will disqualify the material.

**Table 4-2. The chemical composition of the bulk materials expressed as weight percent of major element oxides, total carbon and sulfur of dry mass after ignition. LOI denotes the percent mass loss due to ignition. Wy represents MX-80 bentonite material and the extensions indicate different consignments representing more than 20 years of production. MiR1 represents the IBECO RWC material, Ku40R1 represents the ASHA 229 material and FrR1 represents the Friedland ton material /Karnland et al. 2006/.**

| Material | SiO2  | Al2O3 | Fe2O3 | MgO  | CaO  | Na2O | K2O  | TiO2 | P2O5 | C    | S    | Sum    | LOI   |
|----------|-------|-------|-------|------|------|------|------|------|------|------|------|--------|-------|
| WySt     | 65.9  | 21.5  | 4.46  | 2.82 | 1.63 | 2.69 | 0.56 | 0.24 | 0.06 | 0.51 | 0.37 | 100.7  | 10.40 |
| WyR1     | 68.0  | 21.3  | 3.95  | 2.49 | 1.31 | 2.16 | 0.52 | 0.16 | 0.06 | 0.31 | 0.35 | 100.5  | 9.20  |
| WyR1     | 69.0  | 20.4  | 4.07  | 2.48 | 1.33 | 1.95 | 0.50 | 0.16 | 0.04 | 0.37 | 0.34 | 100.6  | 9.20  |
| WyR1     | 66.3  | 21.7  | 4.32  | 2.71 | 1.61 | 2.38 | 0.61 | 0.18 | 0.03 | 0.33 | 0.36 | 100.5  | 11.90 |
| WyR2     | 67.6  | 21.3  | 4.01  | 2.57 | 1.45 | 2.15 | 0.57 | 0.15 | 0.07 | 0.33 | 0.29 | 100.5  | 9.00  |
| WyR2     | 67.6  | 21.3  | 4.03  | 2.56 | 1.41 | 2.14 | 0.56 | 0.16 | 0.07 | 0.33 | 0.32 | 100.5  | 9.70  |
| Wy mean  | 67.4  | 21.2  | 4.14  | 2.61 | 1.46 | 2.25 | 0.55 | 0.17 | 0.05 | 0.36 | 0.34 | 100.6  | 9.90  |
| STDEV    | 1.13  | 0.45  | 0.20  | 0.13 | 0.14 | 0.26 | 0.04 | 0.03 | 0.01 | 0.07 | 0.03 |        | 1.10  |
| MiR1     | 60.89 | 19.77 | 5.75  | 3.68 | 6.77 | 0.82 | 0.98 | 0.88 | 0.15 | 1.27 | 0.85 | 101.82 | 20.00 |
| KuR1     | 55.76 | 21.63 | 14.75 | 2.16 | 0.87 | 2.32 | 0.14 | 2.19 | 0.06 | 0.18 | 0.11 | 100.17 | 15.40 |
| FrR1     | 66.15 | 18.77 | 6.96  | 2.06 | 0.39 | 1.14 | 3.31 | 1.02 | 0.05 | 0.66 | 0.52 | 101.04 | 7.60  |

**Table 4-3. Results from LECO analyses showing total carbon, organic carbon (T<550°C) and carbonate carbon (T>550°C) in weight% of MX-80 bulk material (WyR1), IBECO RWC (MiR1), ASHA 229 (Ku40R1) and Friedland ton (FrR1) /Karnland et al. 2006/.**

| Material | Total C | Organic C | Carbonate C |
|----------|---------|-----------|-------------|
| WyR1     | 0.38    | 0.20      | 0.18        |
| WyR1     | 0.39    | 0.21      | 0.18        |
| WyR1     | 0.42    | 0.28      | 0.14        |
| WyR1     | 0.40    | 0.25      | 0.15        |
| Mean     | 0.398   | 0.235     | 0.163       |
| STDEV    | 0.017   | 0.037     | 0.021       |
| MiR1     | 1.14    | 0.22      | 0.92        |
| Ku40R1   | 0.26    | 0.22      | 0.04        |
| FrR1     | 0.60    | 0.60      | 0.00        |

**Table 4-4. Results from LECO analyses showing total carbon, organic carbon (T<550°C) and carbonate carbon (T>550°C) in weight% from LOT A2 reference bulk material. The rightmost column shows organic carbon in the purified and ion exchanged clay fractions /Karnland et al. 2009/.**

|           | Bulk material |             |           | Clay fraction |
|-----------|---------------|-------------|-----------|---------------|
|           | Total C       | Carbonate C | Organic C | Organic C     |
| LA2R(1-5) | 0.38          | 0.14        | 0.24      | 0.39          |
| LA2R(1-5) | 0.38          |             |           |               |
| LA2R11    | 0.36          | 0.13        | 0.23      | 0.27          |
| LA2R12    | 0.32          |             |           |               |
| LA2R24    | 0.43          | 0.14        | 0.29      |               |
| LA2R33    | 0.34          | 0.13        | 0.21      | 0.28          |
| LA2R33    | 0.43          |             |           | 0.27          |
| LA2R34    | 0.43          | 0.14        | 0.29      |               |
| mean      | 0.384         | 0.140       | 0.248     | 0.303         |
| STDEV     | 0.043         | 0.007       | 0.033     | 0.067         |

**Table 4-5. Total sulfur, sulfur in sulfate, sulfur in sulfide and maximum possible pyrite content in weight% of MX-80 bulk material (WyR1), IBECO RWC (MiR1), ASHA 229 (Ku40R1) and Friedland ton (FrR1) /Karnland et al. 2006/.**

| Material   | S total | S in sulfate | S in sulfide | max Pyrite |
|------------|---------|--------------|--------------|------------|
| WyR1       | 0.33    | 0.20         | 0.13         | 0.24       |
| WyR1       | 0.38    | 0.22         | 0.16         | 0.30       |
| WyR1       | 0.31    | 0.27         | 0.04         | 0.08       |
| WyR1       | 0.28    | 0.14         | 0.14         | 0.26       |
| WyR1       | 0.39    | 0.23         | 0.16         | 0.31       |
| WyR1 mean  | 0.34    | 0.21         | 0.13         | 0.24       |
| WyR1 STDEV | 0.042   | 0.042        | 0.045        | 0.084      |
| MiR1 mean  | 0.65    | 0.39         | 0.26         | 0.48       |
| Ku40R1     | 0.10    | 0.05         | 0.05         | 0.09       |
| FrR1 mean  | 0.50    | 0.14         | 0.36         | 0.68       |

#### 4.2.2 Mineralogical composition

The sealing properties of a bentonite material are closely related to interaction between the montmorillonite component and water (see Section 2). The main purposes with the mineralogical analyses are therefore to determine the content of montmorillonite and its swelling ability. The composition and distribution of the accessory minerals will largely determine the long term geochemical evolution of the buffer. The mineralogical composition is consequently used as input data in geochemical modeling of the repository. Of special interest is to identify minerals with high solubility, since these will dissolve and diffuse out of the buffer, which would lead to lower buffer density and reduced swelling pressure. The mineralogical composition will further be used for a quantitative check of the chemical composition of the bulk material, and vice versa.

As examples of analyses of mineralogical composition Table 4-6 shows the results from 5 different consignments of MX-80. Table 4-7 shows the mineralogical composition of IBECO RWC, Table 4-8 shows the variation in mineralogical composition of 5 bentonite qualities from Ashapura Mining Company. Table 4-9 shows the mineralogical composition of 4 samples of the Friedland ton material. All results from /Karnland et al. 2006/

The bulk materials were analyzed as random powders by a standard X-ray diffractometer (XRD). The mineral distribution was evaluated by use of an XRD quantitative software based on Rietveld refinement method of least squares fit of calculated to measured XRD profiles. The method is described in general and used for montmorillonite in /Taylor and Matulis 1994/. The accuracy of the measurements differs between minerals and also depends on the character of the sample. A general scrutiny of the quality of an analysis was made by calculation of the total chemical content in the material based on the mineralogical composition. The results were thereafter compared with the actual chemical analysis of the material. The evaluated mean montmorillonite content in four samples taken from a small volume from the same delivery of Wyoming MX-80 bentonite was 83.5% with a standard deviation of 2.2%, which can be regarded as an estimation of the uncertainty in the used method for a high grade bentonite.

The basic mineralogical demand on the buffer material is a montmorillonite content in the range of 75 to 90 percent. No limits are specified for typical accessory minerals, except for the implicit limits set up for the chemical composition, e.g. pyrite and gypsum. It is however a matter of course that highly soluble minerals such as halite cannot be accepted as a significant part of the accessory minerals. Further, significant amounts of non-typical accessory minerals can only be accepted after investigating the consequences. No list of such minerals or limits for their presence has been worked out, since the number of possible minerals is huge, and their presence in commercial bentonites is rare.

**Table 4-6. Results from the XRD analyses of five consignments of the Wyoming MX-80 material. The consignments were delivered around 1980 (WySt), 1995 (WyL1), 1999 (WyL2), 2001 (WyR1) and WyR2). Wym denotes the mean value of the six analyzed samples. The results are expressed as percent of the total mass. Plus and minus denote the maximum deviations from mean values /Karnland et al. 2006/.**

| Phase           | WySt | WyL1 | WyL2 | WyR1 | WyR1m | WyR2 | Wym  | plus | minus |
|-----------------|------|------|------|------|-------|------|------|------|-------|
| Montmorillonite | 82.5 | 79.5 | 79.8 | 82.7 | 83.9  | 80.0 | 81.4 | 2.5  | 1.9   |
| Illite          | 0.7  | 0.8  | 0.7  | 0.8  | 0.8   | 0.7  | 0.8  | 0.1  | 0.1   |
| Calcite         | 1.3  | 0.0  | 0.0  | 0.1  | 0.0   | 0.0  | 0.2  | 1.1  | 0.2   |
| Cristobalite    | 0.2  | 1.4  | 2.5  | 0.6  | 0.7   | 0.0  | 0.9  | 1.6  | 0.9   |
| Gypsum          | 1.4  | 0.7  | 0.9  | 0.7  | 0.8   | 1.1  | 0.9  | 0.5  | 0.2   |
| Muscovite       | 2.4  | 5.1  | 2.6  | 3.5  | 4.4   | 2.5  | 3.4  | 1.7  | 1.0   |
| Plagioclase     | 4.6  | 2.4  | 4.0  | 3.2  | 2.3   | 4.7  | 3.5  | 1.2  | 1.2   |
| Pyrite          | 0.8  | 0.6  | 0.6  | 0.6  | 0.3   | 0.9  | 0.6  | 0.3  | 0.3   |
| Quartz          | 2.6  | 2.5  | 3.8  | 3.0  | 2.8   | 3.2  | 3.0  | 0.8  | 0.5   |
| Tridymite       | 1.7  | 5.0  | 3.8  | 3.9  | 3.1   | 5.1  | 3.8  | 1.3  | 2.1   |

**Table 4-7. Results from XRD analyses of the Milos IBECO RWC material. MiR1m indicate results from the calculated mean diffractogram, and the MiR1 indicate the calculated mean results from all analyses. The results are expressed as percent of the total mass. Plus and minus denote the maximum deviations from mean values /Karnland et al. 2006/.**

| Phase           | MiR1a | MiR1b | MiR1c | MiR1m | MiR1 | Plus | minus |
|-----------------|-------|-------|-------|-------|------|------|-------|
| Montmorillonite | 79.5  | 80.6  | 82.5  | 83.1  | 81.4 | 1.7  | 1.9   |
| Illite          | 5.1   | 4.5   | 4.8   | 4.1   | 4.6  | 0.5  | 0.5   |
| Calcite         | 6.2   | 6.0   | 3.6   | 5.3   | 5.3  | 0.9  | 1.7   |
| Dolomite        | 1.3   | 1.1   | 1.4   | 1.3   | 1.3  | 0.1  | 0.2   |
| Goethite        | 1.5   | 1.7   | 1.4   | 1.4   | 1.5  | 0.2  | 0.1   |
| Muscovite       | 1.4   | 2.1   | 0.7   | 1.3   | 1.4  | 0.7  | 0.7   |
| Pyrite          | 1.2   | 1.2   | 1.0   | 1.0   | 1.1  | 0.1  | 0.1   |

**Table 4-8. Results from the XRD analyses of 5 different bentonite grades from the Ashapura Mining Company. The results are expressed as percent of the total mass /Karnland et al. 2006/.**

| Phase           | Ku36R1 | Ku37R1 | Ku38R1 | Ku39R1 | Ku 40R1 |
|-----------------|--------|--------|--------|--------|---------|
| Montmorillonite | 79.8   | 86.4   | 79.1   | 78.9   | 87.0    |
| Illite          | 10.4   | 0.6    | 1.2    | 1.3    | 1.0     |
| Anatase         | 0.2    | 0.6    | 1.0    | 1.2    | 0.9     |
| Goethite        | 0.7    | 1.3    | 1.4    | 1.0    | 1.3     |
| Gypsum          | 0.3    | 0.7    | 1.4    | 0.6    | 2.2     |
| Maghemite       | 2.7    | 0.4    | 0.7    | 1.4    | 0.4     |
| Microcline      | 0.0    | 0.0    | 0.0    | 1.6    | 0.4     |
| Muscovite       | 0.1    | 2.4    | 4.6    | 2.5    | 0.1     |
| Plagioclase     | 0.2    | 0.6    | 0.5    | 1.8    | 1.0     |
| Pyrite          | 0.9    | 0.5    | 0.5    | 1.1    | 0.3     |
| Quartz          | 0.0    | 1.6    | 3.9    | 0.0    | 0.5     |
| Tridymite       | 0.5    | 1.0    | 1.9    | 3.2    | 2.5     |
| Heulandite      | 2.0    |        |        |        |         |

**Table 4-9. Results from the XRD analyses of 4 samples of the Friedland ton material. The montmorillonite and illite results are adjusted based on the fixed potassium content according to /Karnland et al. 2006/. Values within parenthesis show the original XRD results. FrR1m indicate results from the calculated mean diffractogram, and the FrR1 indicate the calculated mean results from all analyses. The results are expressed as percent of the total mass. Plus and minus denote the maximum deviations from mean values.**

| Phase           | FrR1a     | FrR1b     | FrR1c     | FrR1m     | FrR1      | plus    | minus   |
|-----------------|-----------|-----------|-----------|-----------|-----------|---------|---------|
| Montmorillonite | 34 (34.7) | 29 (32.7) | 25 (30.1) | 32 (35.2) | 30 (33.2) | 4 (2.0) | 5 (3.1) |
| Illite          | 26 (25.5) | 26 (22.7) | 26 (21.0) | 26 (23.2) | 26 (23.1) | – (2.4) | – (2.1) |
| Kaolin          | 8.9       | 13.4      | 8.8       | 11.7      | 10.7      | 2.7     | 1.9     |
| Muscovite       | 6.8       | 6.4       | 10.2      | 5.4       | 7.2       | 3.0     | 1.8     |
| Plagioclase     | 1.2       | 0.8       | 0.2       | 2.3       | 1.1       | 1.2     | 0.9     |
| Pyrite          | 1.4       | 0.9       | 1.7       | 0.9       | 1.2       | 0.5     | 0.3     |
| Quartz          | 18.7      | 20.2      | 22.1      | 19.8      | 20.2      | 1.9     | 1.5     |

### 4.2.3 Cation exchange capacity of bulk material

The cation exchange capacity (CEC) reveals the molar charge of exchangeable ions, which is of importance for the swelling characteristics of the bentonite, and the CEC is thereby a crucial variable. CEC is relatively easy to determine with high precision, and the results may be used to check the evaluated montmorillonite content in the bentonite from the XRD analyses.

Table 4-10 shows results from various number of CEC analyses of 5 different consignments of MX-80 material together with result from one sample of IBECO RWC, Asha 229 and Friedland ton, respectively /Karnland et al. 2006/.

The cation exchange capacity was determined for the bulk material by use of the Cu-trien method described by /Meier and Kahr 1999/. The mean CEC of five samples taken from small volumes from two deliveries of MX-80 bentonite was 0.76 and 0.75 charge equivalents/kg material, respectively (Table 4-10). The standard deviations were 0.02 and 0.01 charge equivalents/kg material, which illustrates the precision of the present Cu-trien method for a high grade bentonite. A minor systematic difference has though been noticed for bentonites dominated by divalent charge compensating ions compared to bentonites dominated by monovalent ions (see Section 4.4.2).

At present, there are no direct acceptance limits for the CEC of the bulk material, but the CEC analyses will be used to check the evaluated montmorillonite content of the buffer material, and the CEC have thereby implicitly acceptance limits.

**Table 4-10. Cation exchange capacity (CEC) of bulk material measured by exchange against Cu(II)-trien. All result in eq/kg. The analyses include five MX-80 samples (Wyxx), one IBECO RWC (MiR1), one Asha 229 (Ku40R1) and one Friedland ton (FrR1) samples.**

|    | Total material<br>Analysis no. | Eq/kg |      |      |      |      | Mean |
|----|--------------------------------|-------|------|------|------|------|------|
|    |                                | 1     | 2    | 3    | 4    | 5    |      |
| US | WySt                           | 0.76  |      |      |      |      | 0.76 |
|    | WyL1                           | 0.75  | 0.76 | 0.78 | 0.78 | 0.74 | 0.77 |
|    | WyL2                           | 0.72  | 0.76 | 0.74 | 0.77 |      | 0.75 |
|    | WyR1                           | 0.74  | 0.75 | 0.76 | 0.76 | 0.76 | 0.75 |
|    | WyR2                           | 0.71  |      |      |      |      | 0.71 |
| Gr | MiR1                           | 0.73  | 0.68 | 0.70 |      |      | 0.70 |
| In | Ku40R1                         | 0.87  | 0.84 |      |      |      | 0.86 |
| Ge | FrR1                           | 0.23  | 0.20 |      |      |      | 0.21 |

#### 4.2.4 Original exchangeable cations

The variable “original exchangeable cations” refers to the amount of each type of the exchangeable cations initially present in the bentonite. Especially the valence of the present cation strongly affects the swelling properties of the bentonite (see Section 2), which in some cases motivates the discrimination of bentonites into Na and Ca-types. The Ca/Na ratio in the bentonite buffer may consequently affect several processes in a repository, such as the course of saturation and the ability to form colloidal particles. Due to the high density of the buffer there is however no difference in sealing properties after full water saturation (see Section 5.1). In the long term perspective, the initial Na/Ca ratio will not play any role since the ground-water conditions will be determinant.

This variable is somewhat complicated to describe both practically and conceptually, since ions from dissolved accessory minerals usually interfere. The magnitude of interference is strongly depending on the type of accessory minerals and of the analyzing technique. By use of an alcoholic solution, the dissolution may be strongly reduced. However, the results will thereby represent the analyzed material in this specific condition. If the same material is immersed in water, e.g. gypsum will dissolve and  $\text{Ca}^{2+}$  will exchange for  $\text{Na}^+$  originally in the montmorillonite. Upon drying, gypsum will again precipitate due to lower solubility compared to sodium sulfate. The variable “originally exchangeable cations” has consequently to be combined with information concerning the mineralogical composition to fully describe a specific condition.

Table 4-11 shows the original exchangeable cations in 5 consignments of MX-80 bentonite. The composition of the original exchangeable ions were determined by exchange against ammonium ions ( $\text{NH}_4^+$ ) in an alcoholic solution in order to reduce dissolution errors due to the presence of e.g. carbonates and sulfates present in the raw bentonite /Belyayeva 1967, Jackson 1975, Polemio and Rhodes 1977/. 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 Cu-CEC-values of the sample. The accuracy is consequently less good than in the CEC analyses, but the analyses of original cations give a clear indication of the dominating cation in the materials.

No specified limits for the variable “original exchangeable cations” have been defined. A high content of potassium or some less common type of exchangeable cation will not be accepted without further investigation.

#### 4.2.5 Grain density

The grain density itself is not of importance for the performance of the buffer. However, the grain density is used as a constant for the evaluation and calculation of the various geotechnical variables such as dry density and degree of saturation. The saturated density limits specified in the Design premises are determined with a specified grain density in mind. Thus, materials with different grain densities require different density intervals to yield the same desired properties.

Grain density is normally determined in a pycnometer according to some geotechnical standard. The conditions for swelling clays are however special since the liquid may or may not interact with the montmorillonite depending on the liquid in use. Kerosene has traditionally been used because

**Table 4-11. Exchangeable cations in five consignments of MX-80 bulk materials. /Karnland et al. 2006/.**

| Sample | eq/kg |       |       |       |       | % charge |      |      |      |
|--------|-------|-------|-------|-------|-------|----------|------|------|------|
|        | Ca    | Mg    | K     | Na    | Sum   | Ca       | Mg   | K    | Na   |
| WySt   | 0.08  | 0.05  | 0.01  | 0.67  | 0.80  | 9        | 6    | 2    | 83   |
| WyL2   | 0.14  | 0.04  | 0.01  | 0.49  | 0.68  | 21       | 6    | 2    | 71   |
| WyR1   | 0.15  | 0.06  | 0.02  | 0.57  | 0.80  | 18       | 8    | 2    | 72   |
| WyR1   | 0.11  | 0.04  | 0.01  | 0.54  | 0.71  | 15       | 6    | 2    | 77   |
| WyR1   | 0.11  | 0.05  | 0.01  | 0.53  | 0.71  | 16       | 7    | 2    | 75   |
| WyR2   | 0.15  | 0.05  | 0.01  | 0.49  | 0.70  | 21       | 7    | 2    | 71   |
| mean   | 0.13  | 0.05  | 0.01  | 0.55  | 0.73  | 17       | 6    | 2    | 75   |
| STDEV  | 0.026 | 0.006 | 0.003 | 0.060 | 0.047 | 3.96     | 0.57 | 0.27 | 4.40 |



it has a low interaction with the clay material, which is preferable from a practical point of view, i.e. it will not make a mess. However, kerosene is not used in this case, since the very purpose with the bentonite buffer is to interact with water and the two liquids give different grain density results (Figure 4-1). The difference is discussed more in detail in /Karnland et al. 2006/. A saline solution is instead used because water thereby separates the individual montmorillonite layers, but the salinity reduces the swelling and thereby facilitates the measurement. The difference in measured grain density between the two liquids is relatively small in the Friedland ton material (FrR1) as a consequence of the low montmorillonite content.

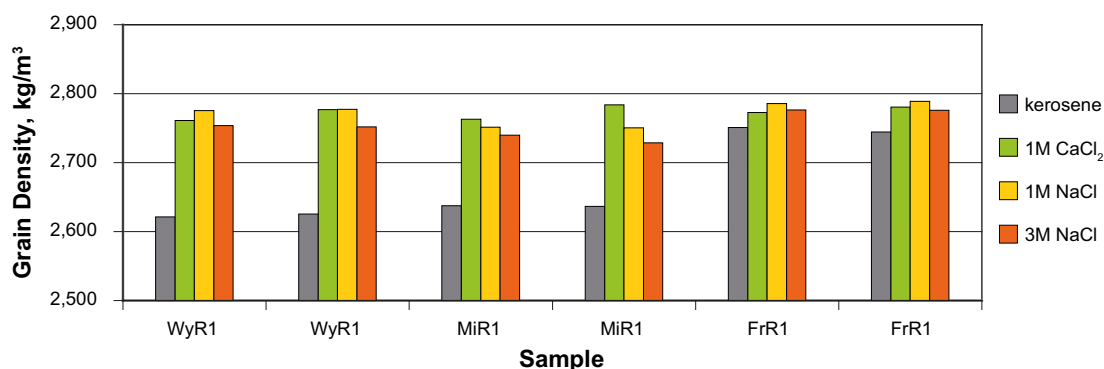
The grain density of the reference bentonite MX-80 (WyR1) and the IBECO RWC material (MiR1) are rather similar and lies in the interval 2,750 to 2,780 kg/m<sup>3</sup> based on the results from the NaCl solutions. The Buffer Production report uses the value 2,750 kg/m<sup>3</sup>.

#### 4.2.6 Specific surface area

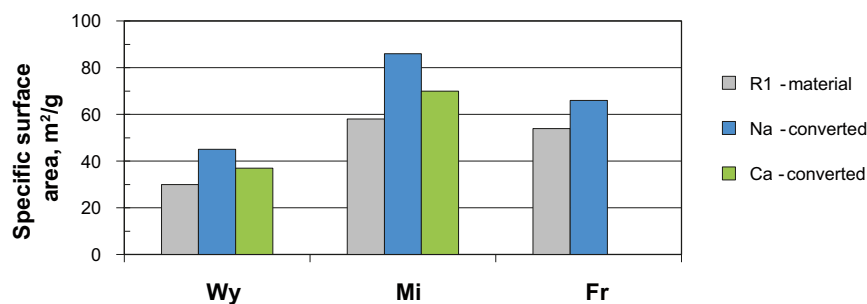
There is no direct information from BET results which is relevant for discriminating different bentonites as buffer material. The measurements are though relatively simple to perform and are often used in soil science. BET measurements will therefore still be performed in order to get an as complete buffer material characterization as possible.

Figure 4-2 shows results from specific surface area analyses of MX-80, IBECO RWC and Friedland ton determined by use of standard BET technique and a Micrometrics ASAP 2400 instrument.

Typically, the measured specific surface area by use of nitrogen gas gives results in the range of 20 to 100 m<sup>2</sup>/gram clay regardless of the preparation technique and montmorillonite content. Comparison with the total theoretical surface area of montmorillonite of around 750 m<sup>2</sup>/gram indicate that the dry material is dominated by montmorillonite layers in close contact, and that the interlayers are inaccessible for the nitrogen gas.



**Figure 4-1.** Results from grain density determinations of the MX-80 (WyR1), IBECO RWC (MiR1) and Friedland ton (FrR1) bulk materials performed in kerosene, 1.0 M and 3.0 M NaCl solutions, and 1.0 M CaCl<sub>2</sub> solution /Karnland et al. 2006/.



**Figure 4-2.** BET specific surface area results for MX-80 material (Wy), IBECO RWC material (Mi), and Friedland material (Fr), respectively. All three materials were analyzed as delivered (R1-material), after purification and ion exchange to sodium state (Na-converted), and the Wy and Mi material were also ion exchanged to calcium state (Ca-converted) /Karnland et al. 2006/.

#### 4.2.7 Grain size

Grain size of soil materials may be split in at least two different concepts. One being the size of the grains which are conglomerates of smaller particles, only held together under dry or semi-dry conditions, i.e. in common language a clod of earth. The other concept is the size of the fundamental particles, which usually is analyzed after dispersion of the material in water and some dispersion agent (e.g. sodium pyrophosphate). The difference is negligible for many soils, but for bentonite materials the difference is essential since the basic montmorillonite particles always stick together under dry and semidry conditions, but disperse in contact with water (see Section 4.2.6).

The size distribution of the “clod grains” is of importance for the air evacuation during block production and in order to avoid dust problems, but has no effect on the long-term function of the buffer. The “clod grain” size distribution is analyzed by dry-sieving. The “clod grain” size may be controlled technically by milling or granulation and is not further considered here.

The fundamental (dispersed in water) particle size distribution is of interest because the particle size has relevance for the chemical reactivity of the accessory minerals. The montmorillonite particles are however always smaller than the resolution of a standard sedigraph. The main purpose is therefore to get an independent check of the content of montmorillonite, which always will be found in the clay fraction (particle size < 2 μm). No limits are specified, but in case the clay fraction is less than the montmorillonite fraction, further analyses are necessary.

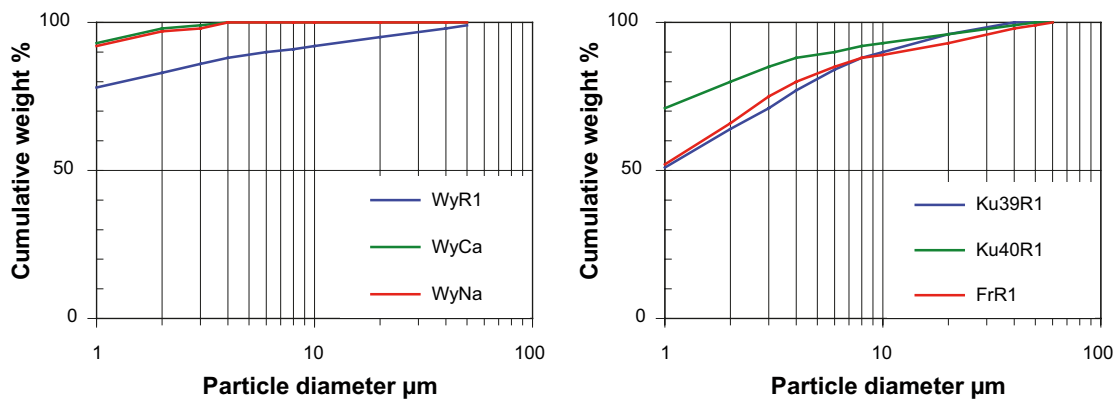
Figure 4-3 shows the fundamental (dispersed in water) particle size distribution of MX-80 reference material and after purification and ion-exchange to Na and Ca-state, two Asha bentonites and Friedland ton. A Sedigraph 5000 ET particle analyzer (Micromeritics) was used. The bulk samples were dispersed in 0.5% sodium pyrophosphate by ultra-sonic treatment for 15 minutes and left on a magnetic stirrer for at least 2 hours prior to analysis. The Na-saturated and dialyzed samples were dispersed in de-ionized water only.

#### 4.3 Water content

The water content ( $w$ ), sometimes referred to as water ratio, is defined as:

$$w = \frac{m_w}{m_s} \quad \text{Equation 4-1}$$

Where  $m_w$  is the mass of water and  $m_s$  is the mass of solids. This variable has relevance in a number of processes, but has no relevance for discriminating between different bentonites. It is though determined for economic reasons since the price of bentonite generally is based on delivered total mass. For compaction of the bentonite blocks water will be controlled, and there is consequently no need for specific limits of delivered bentonite as long as the bentonite is possible to handle.



**Figure 4-3.** Grain size distribution of the Wyoming MX-80 bulk material and the purified and the corresponding ion-exchanged calcium and sodium materials (left). Grain size distribution of bulk material of two Asha bentonites (Ku39R1 and KU40R1) and Friedland ton (FrR1) (right) /Karland et al. 2006/.

Water content is determined by a standard geotechnical method. The sample is dried in a ventilated oven at a temperature of 105°C for 24 hours, and the mass loss of water is determined by a laboratory balance. The precision of the analyses may be adjusting to the actual needs by changing the sample size and/or the precision of the balance.

## 4.4 Montmorillonite composition

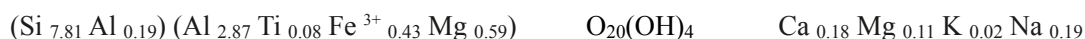
### 4.4.1 Structural formula of the montmorillonite

The structural formula of the montmorillonite component is of interest since it, first of all, shows that the mineral in question really is montmorillonite. The formula further may be used in calculating the chemical composition of all minerals, which in turn may be used to confirm the measured chemical composition (see Section 4.2.1). The formula gives information concerning the precise position of involved elements and Fe(II)/Fe(III) ratio, which may be relevant for the chemical/mineralogical evolution of the buffer.

The chemical composition of a Na-exchanged clay fraction (grain size < 2 µm) was analyzed for major elements, using standard ICP/AES technique. The results were used to calculate the structural formula in accordance with /Newman and Brown 1987/ with the additional compensation for fixed potassium. Further details are given in /Karnland et al. 2006/. The measured mean molar weight of the montmorillonite in the MX-80 material, based on an O<sub>20</sub>(OH)<sub>4</sub>-unit, was 741 grams. The mean layer charge was -0.60, of which 10% was situated in the tetrahedral sheets. The mean structural formula for the montmorillonite was:



The measured mean molar weight of the montmorillonite in the IBECO RWC material, based on an O<sub>20</sub>(OH)<sub>4</sub>-unit, was 739 grams. The mean layer charge was -0.78, of which 24% was situated in the tetrahedral sheets. The mean structural formula for the montmorillonite was:



The specified limits for the variable montmorillonite composition is that the layer charge should fall within the range for montmorillonite (0.4 to 1.2 unit charges per O<sub>20</sub>(OH)<sub>4</sub>-unit) and that the dominating charge should emanate from the octahedral sheet.

### 4.4.2 Cation exchange capacity of the clay fraction

The variable “CEC of the clay fraction” has an important control function. The CEC should correlate with the calculated CEC of the montmorillonite composition and with the CEC of the bulk material after taking the montmorillonite content into account.

The cation exchange capacity (CEC) was determined by use of the Cu-trien method described by /Meier and Kahr 1999/. The method gives a minor systematic difference in measured CEC depending on the valence of the charge compensating ions even if the original material is the same. The reported CEC results were therefore determined on the clay fraction after ion exchange to Na<sup>+</sup> in order to facilitate comparison with the montmorillonite structural formula and between different samples.

The mean CEC of five clay fraction samples extracted from the same bulk MX-80 sample was 0.86 charge equivalents/kg material according to /Karnland et al. 2006/. The standard deviation was 0.02 eq/kg, which indicates the uncertainty of the method. The mean CEC result was 0.82 eq/kg for the of the IBECO RWC clay fraction, 0.88 eq/kg for the Asha 229 clay fraction, and 0.34 eq/kg for the Friedland ton clay fraction.

## 5 Coupling between bentonite mineralogy and the sealing properties

### 5.1 General

The sealing properties of a specific bentonite material are strongly dependent on the mass of bentonite per volume, and several density describing variables are commonly used. Saturated density ( $\rho_m$ ) has e.g. been used in the dimensioning of the reference bentonite buffer since it is intuitive for a fully water saturated material. The term saturated density refers to the bulk density of the material when full water saturation is reached, i.e. when all pores are water-filled. Saturated density is consequently defined as:

$$\rho_m = \frac{m_{solids} + m_{max\ water}}{V_{total}} \quad \text{Equation 5-1}$$

Where  $m_{solids}$  is the mass of the solids,  $m_{max\ water}$  is the maximum possible mass of water, and  $V_{total}$  is the total volume of all components (solids and water in this case).

Alternative variables to illustrate principally the same information are dry density ( $\rho_d$ ), void ratio ( $e$ ), porosity ( $n$ ) and water content (sometimes referred to as water ratio) at full saturation ( $w_m$ ).

Dry density ( $\rho_d$ ) is defined as: 
$$\rho_d = \frac{m_{solids}}{V_{total}} \quad \text{Equation 5-2}$$

Void ratio ( $e$ ) is defined as: 
$$e = \frac{V_{void}}{V_{solids}} \quad \text{Equation 5-3}$$

Where  $V_{void}$  is the total volume of voids (water filled or not) and  $V_{solid}$  is the volume of all solids.

Porosity ( $n$ ) is defined as: 
$$n = \frac{V_{void}}{V_{total}} \quad \text{Equation 5-4}$$

These variables are commonly used also for semi and fully water saturated systems in combination with additional information on the degree of saturation.

Water content (or water ratio) at full saturation ( $w_{sat}$ ) is defined as:

$$w_{sat} = \frac{m_{max\ water}}{m_{solids}} \quad \text{Equation 5-5}$$

Regardless of which of the above variables that is used, the relation to any sealing property is specific for the material in question and not relevant for bentonites in general (Figure 5-1 and Figure 5-2). Replacing e.g. the volume of an accessory mineral like feldspar by the same volume of a heavy mineral, such as barite, will obviously increase the density, but will not affect the swelling pressure or hydraulic conductivity. And the opposite, a change in montmorillonite content will change the sealing properties but not the density if the grain density of the replacing mineral is the same as that of the montmorillonite.

In order to have a more general description of the sealing properties, the effective montmorillonite dry density ( $\rho_{d\ mont}$ ) has been defined as /Dixon et al. 2002/:

$$\rho_{d\ mont} = \frac{m_{mont}}{V_{voids} + V_{mont}} \quad \text{Equation 5-6}$$

Where  $m_{mont}$  and  $V_{mont}$  represents the mass and volume of the montmorillonite, respectively. The effective montmorillonite dry density may then be used also for comparison between different bentonites, assuming that the montmorillonite components in the bentonites are relatively similar, and that the accessory minerals may be considered an inert filler. In other words, only the ratio between water and montmorillonite determines the properties under these assumptions.

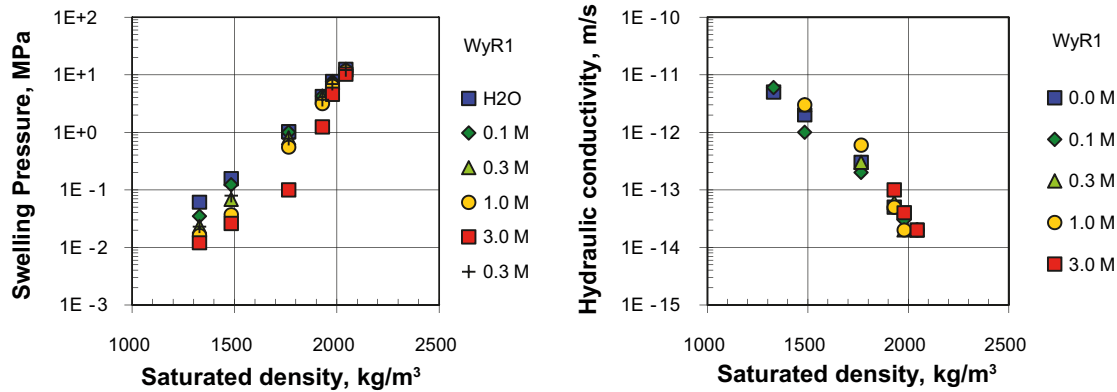


Figure 5-1. Swelling pressure (left) and hydraulic conductivity (right) in the Wyoming MX-80 reference material (WyR1) versus saturated bentonite density /Karnland et al. 2006/. The legends show the NaCl concentrations in the test solutions in successive contact with the WyR1 test sample.

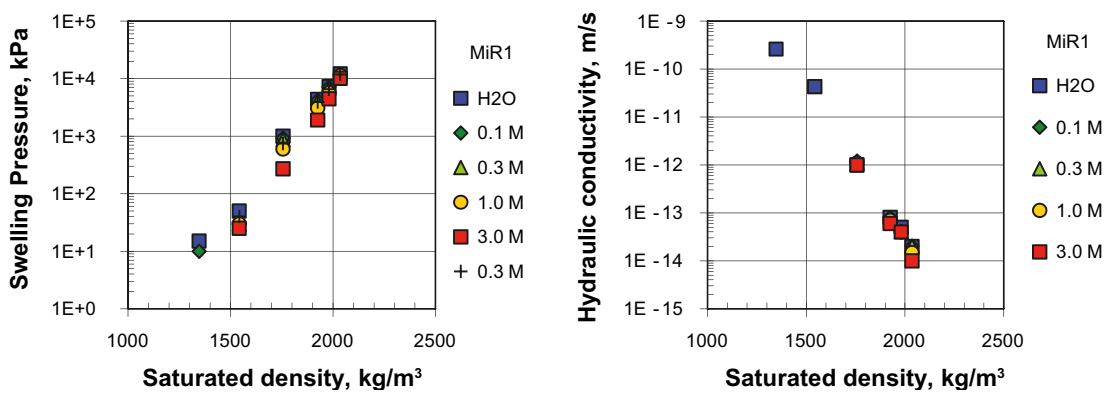


Figure 5-2. Swelling pressure (left) and hydraulic conductivity (right) in the IBECO RWC reference material (MiR1) versus saturated bentonite density /Karnland et al. 2006/. The legends show the NaCl concentrations in the test solutions in successive contact with the MiR1 test sample.

In this context we may limit the discussion to only swelling pressure based on the following arguments. It is an experimental fact that hydraulic conductivity ( $k$ ) is closely related to swelling pressure ( $P_s$ ) according to:

$$P_s = c \cdot k \quad \text{Equation 5-7}$$

where  $c$  is a constant which is almost the same for high grade bentonites /Karnland et al. 2006/. The relation is valid for a rather wide range of pressure-conductivity results, which well cover the conditions in a repository. For the two reference bentonites MX-80 and IBECO RWC the constant ( $c$ ) is between  $1E-7$  and  $5E-7$  for  $P_s$  expressed in Pa and k in m/s.

The construction premise for the variable hydraulic conductivity is fulfilled if  $k < 10^{-12}$  m/s (see Section 3). According to Equation 5-7, this corresponds to a minimum swelling pressure of 500 kPa for the most pessimistic value of the constant  $c$ . This is consequently 4 times lower than the demand of a swelling pressure of at least 2 MPa in order to prevent bacterial activity. The request on low hydraulic conductivity can thereby be expected to be fulfilled if the request on swelling pressure is fulfilled.

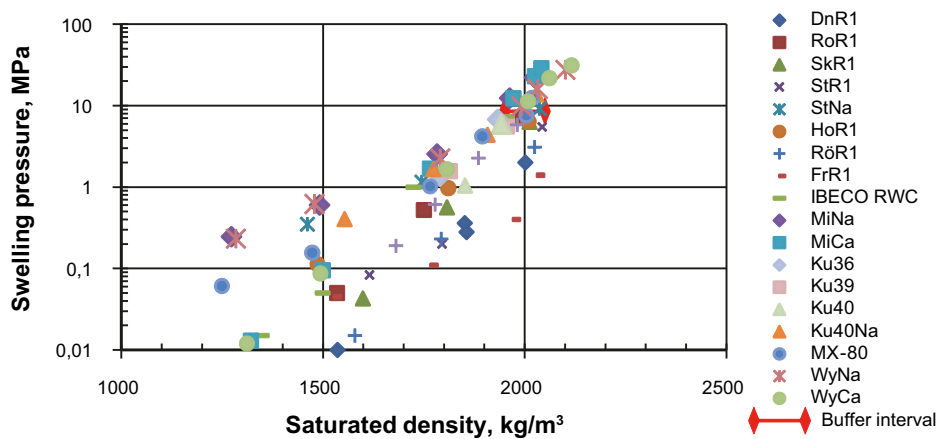
## 5.2 Swelling pressure

Figure 5-3 shows the swelling pressure of a number of pure montmorillonites, bentonites and swelling clays plotted against density at full water saturation /Karnland et al. 2006/. For an individual material it is obvious that the impact of density is of major importance for the swelling pressure. However, the variation in swelling pressure between the different materials at the same density is more than one order of magnitude, and density alone does apparently not fully describe the variation in swelling pressure as discussed in Section 5.1.

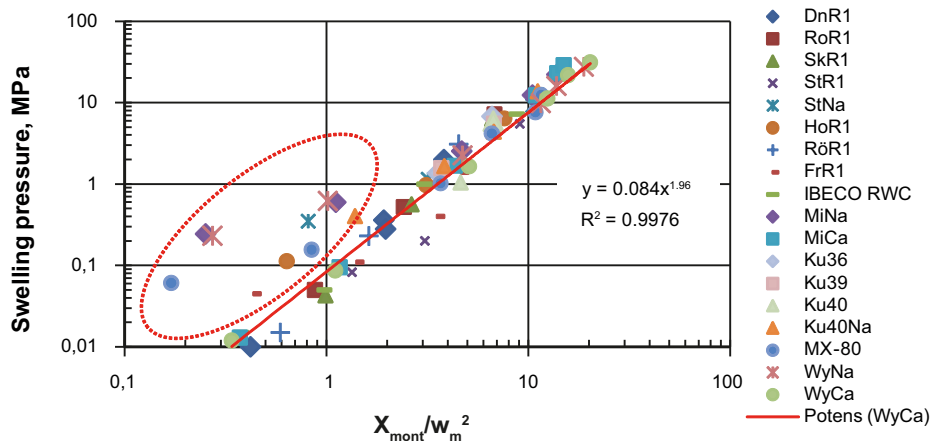
The content of swelling mineral in the various materials is of course of major importance for the swelling pressure. In the examined materials, this content is expressed as montmorillonite content ( $X_{mont}$ ) defined as:

$$X_{mont} = \frac{m_{mont}}{m_{solids}} \quad \text{Equation 5-8}$$

The correct description in some of the materials should rather be beidellite, but the difference is not considered here since the layer charge range is the same as for montmorillonite (see Section 2). As discussed in Section 5.1 the density may be a relevant variable for a specific material but not for a more general description of swelling pressure. Therefore, the montmorillonite content ( $X_{mont}$ ) and the water content at full saturation ( $w_{sat}$ ) are used here as investigating variables, since swelling pressure is a consequence of interaction between these components, and since they are experimentally determined (see Section 4.2.2 and 4.3). In Figure 5-4, all the measured swelling pressures shown



**Figure 5-3.** Measured swelling pressure for a number of bentonites and swelling clay materials plotted against water saturated density of the materials /Karnland et al. 2006/. The red bar indicate the specified buffer density interval relevant for the two reference bentonites MX-80 and IBECO RWC.



**Figure 5-4.** All measured swelling pressures in Figure 5-3 plotted against the new variable based on montmorillonite content ( $X_{mont}$ ) and water content at full water saturation ( $w_{sat}$ ).

in Figure 5-3 are plotted against the new variable  $X_{mont}/(w_{sat})^2$ . The  $Ca^{2+}$  dominated materials are thereby fairly well aligned over the whole examined density interval, which is indicated by the unbroken line. In the low pressure region, the  $Na^+$  dominated materials have higher pressures, indicated by the dotted ellipse. This deviation may conceptually be explained by the well documented osmotic pressure component in  $Na^+$  bentonites, which can be quantified by use of the DLVO theory (Figure 5-5). However, there is no significant difference between the  $Na^+$  and  $Ca^{2+}$ -materials in the high pressure region, which is representative for the buffer material. The remaining scatter in pressure results around the red line in Figure 5-4 may be attributed to the accuracy in measured values of water content, montmorillonite content and swelling pressure, and to other potential variables which may affect the swelling pressure such as magnitude of layer charge and charge distribution between octahedral and tetrahedral positions. It should also be mentioned that there is hysteresis in the relation between any type of density describing variable and swelling pressure, i.e. any given density may result in different swelling pressure depending on the pressure-volume history of the material /Börgesson et al. 1988/. This effect is however relatively small in comparison with the density effect.

The alignment around the red line in Figure 5-4 indicates that the measured relation between the variable  $X_{mont}/(w_{sat})^2$  and swelling pressure is of the type  $f(x) = B \cdot x^a$  in this presentation. The slope shows that the constant ( $a$ ) has a value close to 2. An expression for swelling pressure in bentonites dominated by divalent exchangeable ions may consequently be formulated based on these rather extensive experimental data:

$$P_s = B \cdot \left( \frac{X_{mont}}{(w_{sat})^2} \right)^a \quad \text{Equation 5-9}$$

The expression is valid also for the examined sodium bentonites in the high pressure region, which is relevant for the bentonite buffer.

Equation 5-9 may be rewritten in the following way:

$$P_s = B \cdot \frac{\left( \frac{m_{mont}}{m_{solids}} \right)^a}{\left( \frac{m_{water}}{m_{solids}} \right)^{2a}} \quad \text{Equation 5-10}$$

$$P_s = B \cdot \frac{(m_{mont})^a \cdot (m_{solids})^a}{(m_{water})^{2a}} \quad \text{Equation 5-11}$$

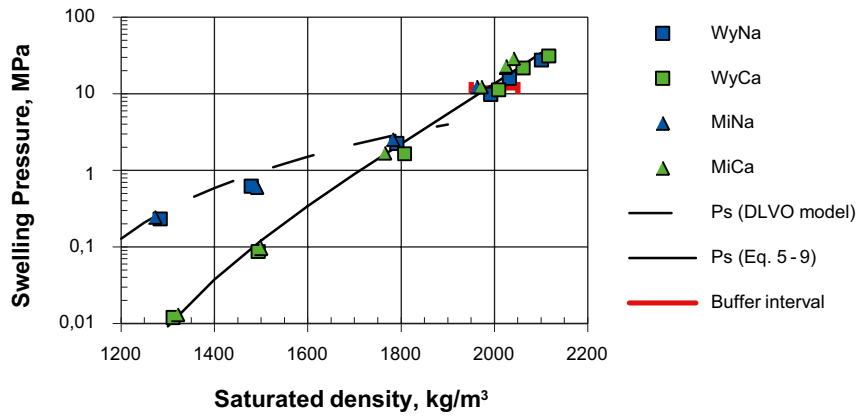
$$P_s = B \cdot \frac{(m_{mont})^a \cdot (m_{mont} + m_{acc})^a}{(m_{water})^{2a}} \quad \text{Equation 5-12}$$

$$P_s = B \cdot \frac{(m_{mont})^{2a} \cdot \left(1 + \frac{m_{acc}}{m_{mont}}\right)^a}{(m_{water})^{2a}} \quad \text{Equation 5-13}$$

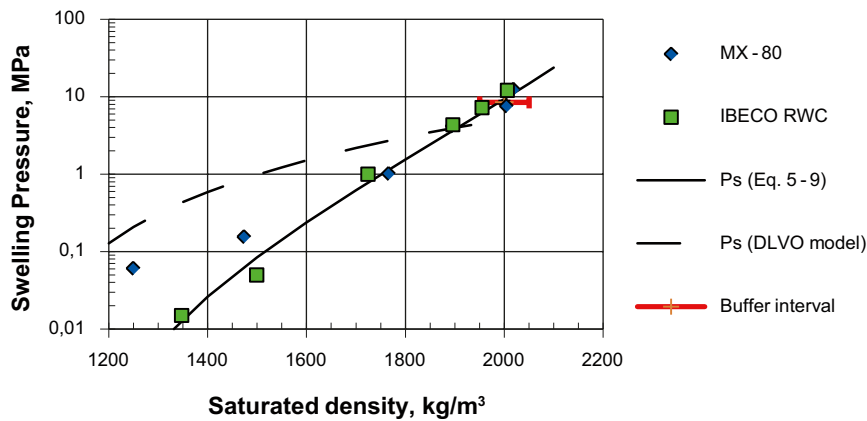
Where  $m_{acc}$  is the mass of the accessory minerals.

Equation 5-13 shows that the assumption that accessory minerals may be considered inert filler is not fully correct since there obviously is an effect of accessory minerals. For the low grade bentonites this effect is pronounced, but for high grade bentonites, such as the MX-80 and IBECO RWC bentonites, the effect is so small that it cannot be revealed by the present set of data. For the purified and  $Ca^{2+}$ -exchanged MX-80 material (WyCa), the constant ( $a$ ) takes the value 1.96 and ( $B$ ) takes the value 0.084.

Figure 5-5 shows measured (dots) swelling pressure results versus saturated density for pure montmorillonites based on MX-80 (WyNa, WyCa) and IBECO RWC (MiNa, MiCa) reference bentonites after purification and ion exchange to  $Na^+$  and  $Ca^{2+}$  states, respectively. The dotted line shows calculated pressures according to DLVO theory, and the unbroken line shows calculated pressures by use of Equation 5-9 and the evaluated values for ( $a$ ) and ( $B$ ) for the purified and Ca-converted MX-80 material. Figure 5-6 shows measured swelling pressures of the reference bentonites MX-80 and IBECO RWC as a function of saturated density. The line represents the calculated swelling pressures according to Equation 5-9 and the evaluated constants for the purified and Ca-converted MX-80 material.



**Figure 5-5.** Measured swelling pressures in purified montmorillonites based on MX-80 and IBECO RWC reference bentonites after ion exchange with  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , respectively. The dotted line indicates calculated pressures based on DLVO theory. The unbroken line indicates calculated pressures based on the empirical model according to Equation 5-9. The red bar indicates the acceptable density interval in the KBS-3 repository.



**Figure 5-6.** Measured swelling pressures in the reference bentonites MX-80 and IBECO RWC as a function of saturated density. The line indicates calculated swelling pressures according to Equation 5-9 and measured values for the montmorillonite content of MX-80. The red bar indicates the acceptable density interval in the KBS-3 repository. Note that experimental MX-80 data are partly covered by the IBECO RWC data.

By use of the empirical model (Equation 5-9) and evaluated constants for the purified and Ca-converted MX-80 material, the following pressure variations are calculated for the reference bentonite MX-80. The stipulated montmorillonite content interval from 0.75 to 0.9 gives a pressure range from 8 to 11 MPa at the nominal saturated density 2,000 kg/m<sup>3</sup>. The stipulated saturated density interval 1,950 to 2,050 kg/m<sup>3</sup> gives a pressure range from 6 to 15 MPa at the measured montmorillonite content 0.83. The combined effects of the stipulated montmorillonite content interval and saturated density interval lead to a pressure range of 5 to 17 MPa. If the effect of accessory minerals is not taken into account then the combined pressure range is 3 to 14 MPa.



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