Technical Report

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Is montmorillonite-rich clay of MX-80 type the ideal buffer for isolation of HLW?

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ABSTRACT

Four commercial clays, saponite, mixed-layer smectite-mica, kaolinite, and palygorskite, have been examined as possible alternatives to MX-80 buffer. General estimates based on the microstructural constitution and hydration potential as well as actual laboratory testing show that except for normally graded kaolinite, they would all serve acceptably in a repository. MX-80 is, however, superior with respect to hydraulic conductivity and retardation of diffusive transport of relevant cations and, like saponite and palygorskite, it has a high swelling pressure, that may in fact be too high. The mixed-layer clay is less but sufficiently expandable and is concluded to have better thermal and rheological properties as well as gas release capacity. It is hence the number one competitor to MX-80.

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SAMMANFATTNING

Som buffertlera, dvs det täta jordmaterial som skall omge HLW-kapslarna för att minimera vattenflöde och diffusiv jontransport i kapslarnas omgivning och ge mekaniskt stöd åt dem enligt KBS3-konceptet, föreslås sedan många år montmorillonitrik lera, MX-80, med hög densitet. Rapporten ger besked om att flera lertyper, saponit (Mg-rik smektit), mixed-layer smektit-glimmer, och palygorskit ger acceptabelt låg vattengenomsläpplighet vid den densitet som uppnås vid kompaktering av respektive lerpulver under 100 MPa tryck och det är sannolikt att detta också gäller kaolinit om den framställs i mycket finkornig form. MX-80 är överlägsen i detta avseende på grund av sin starka vattenbindnings- och gelbildningsförmåga. Fördröjning av vissa betydelsefulla katjoners transport genom diffusion åstadkoms också bäst av MX-80 medan finmald kaolinit kan fördröja anjontransport mest effektivt. Svällningsförmågan och svällningstrycket är högst hos MX-80, saponit och palygorskit medan de är lägre för mixed-layerleran och försumbara för normalgraderad kaolinit. Svällningstrycket är mycket känsligt för små densitetsändringar och kan bli alltför högt för MX-80, saponit och palygorskit men det är lägre och sannolikt tillräckligt hos mixed-layerleran. Värmeledningsförmågan hos den sistnämnda lertypen är bäst och den uppvisar också de bästa reologiska egenskaperna. Sammantaget bedöms den montmorillonitrika MX-80 leran liksom saponitleran fungera väl både när det gäller den kemiska stabiliteten och den fysikaliska funktionen men buffert av mixed-layermineral, representerad av Friedlandlera i denna studie, är en stark konkurrent.

SUMMARY

The buffer clay, i.e. the canister-embedding dense soil material that is intended to minimize flow and diffusive ion transport in the vicinity of the canisters and to provide mechanical support to them according to the KBS3 concept, is currently proposed to be the montmorillonite-rich, commercial bentonite MX-80. The report claims that several other clay types, saponite (Mg-rich smectite), mixed-layer smectite-mica, and palygorskite have an acceptably low hydraulic conductivity for the density that can be obtained by compacting the respective clay powders under 100 MPa pressure and this is probably also valid for very fine-grained kaolinite. MX-80 is superior in this respect due to its strong hydrophilic and gel-forming capacities and MX-80 also offers the most effective retardation of the transport of certain important cations, while very fine-grained kaolinite has the best ability to retard anion transport. The expandability and swelling pressure are highest for MX-80, saponite and palygorskite while they are lower for the mixed-layer clay and negligible for normally graded kaolinite. The swelling pressure is very sensitive to small density changes and may be too high for MX-80, saponite and palygorskite while it is lower but probably sufficient for the mixed-layer clay. Its heat conductivity and rheological behavior are superior. In summary, MX-80 and the saponite would work well both chemically and physically but the mixed-layer clay, represented by the Friedland clay in the present study, is a strong competitor.

1 INTRODUCTION

Montmorillonite-rich clay in the form of commercial MX-80 bentonite manufactured by American Colloid, USA, was proposed some 20 years ago as suitable buffer clay material for SKB. Its general properties fulfilled the criteria defined at that time with respect to tightness, expandability and rheological behavior and it has served as reference buffer material and clay component in backfills in shafts and tunnels since that time. Most of SKB:s research on buffer and backfills has been made using this type of clay but other smectitic clays have been tested on a smaller scale to get an overall picture of the variation in physical properties generated by different contents and compositions of smectite clay.

It has been found that among the smectites, of which the iron-rich species nontronite is too sparsely represented in nature to be of practical interest and the aluminous beidellite too easily converted to non-expandable illite to be accepted, only montmorillonite and the magnesium-rich saponite qualify. A more detailed comparison between these two clays has not yet been made, nor have other potentially useful clay types, like palygorskite, kaolinite and mixed-layer minerals, been examined. The present report provides data for comparison of all these clay species.

2 BUFFER CLAY CANDIDATES

Montmorillonite, a clay mineral that belongs to the smectite group, is currently proposed as major component of buffer clay because it provides a low hydraulic conductivity and a strong expandability. However, in certain respects it is not as good as some other clay minerals and it is therefore important to examine these for assessing how useful they may be in comparison with montmorillonite.

Only clay minerals that are available in large quantities and relatively high concentrations are of interest in the present context, which hence excludes potentially interesting but relatively rare minerals like hectorite and nontronite, and minerals appearing in large amounts but low concentrations like glauconite and illite . This study is therefore confined to deal with the following minerals:

- Saponite (smectite species)
- Mixed-layer (smectitic)
- Kaolinite
- Palygorskite (attapulgite)

A major issue in the report is to compare the physical properties of clays consisting of these minerals and of montmorillonite in the form of commercial MX-80 clay.

Assessment of the various clay mineral candidates requires comparison of their major properties but also confirmation that they fulfil the criteria that have been set, i.e.:

- The buffer should give the canister favorable environment for maintaining the isolation, comprise a protective layer between the canister and the rock with respect to mechanical and chemical processes, and, if the isolation fails, limit and retard the escape of radionuclides from the repository.

- Protection level 1: Completely embed the canister for a long time (>10 000 years), bear the canister, prevent groundwater flow in the deposition hole, retard inward transport of corrodants, dissipate heat from the canister, resist chemical transformation, allow canister and rock to perform acceptably, protect the canister from tectonics, and filter colloids.

- Protection level 2: Retard transport of radionuclides by minimizing flow through the buffer and offering sorption by the buffer.

These criteria imply that the creep strain should be small, which is fulfilled in principle if the clay is low-plastic and behaves as a frictional material. Also, the transport of radionuclides through the buffer by porewater flow must be less than by diffusion. In practice this usually means that the conductivity should be lower than E-11 m/s.

3 CHARACTERIZATION

3.1 Clay materials

The investigated clays were the following:

1. Saponite, Madrid area, Spain.
2. Mixed-layer smectitic mineral, Mecklenburg/Vorpommern, Germany.
3. Kaolinite, Sachsen, Germany.
4. Palygorskite, Greece.

According to the manufacturers' information the respective soil materials are available in large quantities, i.e. several million tons.

3.2 Occurrence and use

Saponite

Saponite, which has been frequently used as drilling mud and in the ceramic industry, is present in many soil horizons in various parts of the world. Exploitable deposits are frequent in Mexico, Ukraine and Spain. The material investigated in the present study originated from Cerro del Aguila in the Madrid basin [1]. The amount of raw material in this and similar deposits is estimated at several millions of tons.

Mixed-layer smectite-illite

One of the largest well characterized deposits of uniform smectitic mixed-layer soil in Europe is the Friedland clay in the Neubrandenburg area in Mecklenburg/ Vorpommern, north-eastern Germany [2]. It represents at least 10^8 tons and has been extensively used for tile production and for sealing of shallow waste piles and is taken as representative of expandable mixed-layer clays here. Another example is the randomly ordered mixed-layer kaolinite/smectite clay from the Paris basin. It is termed Fo-Ca 7 [3]. Since the German clay has been exploited for a long time and is known to make up a huge deposit with very small variations in composition it is selected for the present study.

Kaolinite

Kaolinite-rich material, which is essential for the paper and ceramic industries, is found in large amounts in many parts of the world. Deposits of rather pure kaolinite are exploited in southeastern United States, China, Japan, Nigeria and the British isles and also in France and Germany. Each of them contains several million tons of raw material. In Sweden homogeneous kaolinite clays are present in Skåne where a deposit comprising at least 1 million tons raw material is presently being exploited. The material investigated in the present project stems from Lagerstätten imRaum Kemmlitz in Sachsen, Germany, where there are considerably larger deposits.

Palygorskite

Historically, the pre-Columbian indians in the Yucatan Peninsula, Mexico, manufactured the famous pigment ”Maya Blue” with palygorskite and indigo and used this mineral in pottery [4]. The most important presently exploited North American deposits of palygorskite are in the Attapulgus-Quincy district of Georgia and Florida.

Ukrainian deposits in the Cherkassk area south of Kiev have been reported to contain large amounts (4-5 million tons) of palygorskite [5]. Other major deposits are those in Australia and the Andhra Pradesh district, India.

In Europe, wellknown, rich deposits are those in the Madrid (Tajo) basin, the Lebrija deposit near Cadiz, and in the Paris basin in France. Recently, Greek deposits that are very rich in palygorskite have been identified and examined as reported here [6].

Montmorillonite

Montmorillonite in the form of natural or ion-exchanged bentonites is proposed as major clay mineral constituent of the buffer clay by several organizations like SKB, POSIVA, ENRESA, and JNC. It is available in large quantities in all parts of the world [7] and is widely used in the industry for pelletization, stabilization of moulding-sand, cosmetics, and preparation of drilling muds. In the present study, a commercial brand, MX-80, which is a natural Na-dominated bentonite and SKB:s reference buffer material, is used as a standard measure.

MX-80 has been described in numerous SKB reports with respect to its composition and physical properties and particularly to its chemical stability under repository conditions [8,9,10].

3.3 Crystal constitution, particle size, specific surface area

The crystal structure of the three clay mineral types considered here is shown in Figure1.

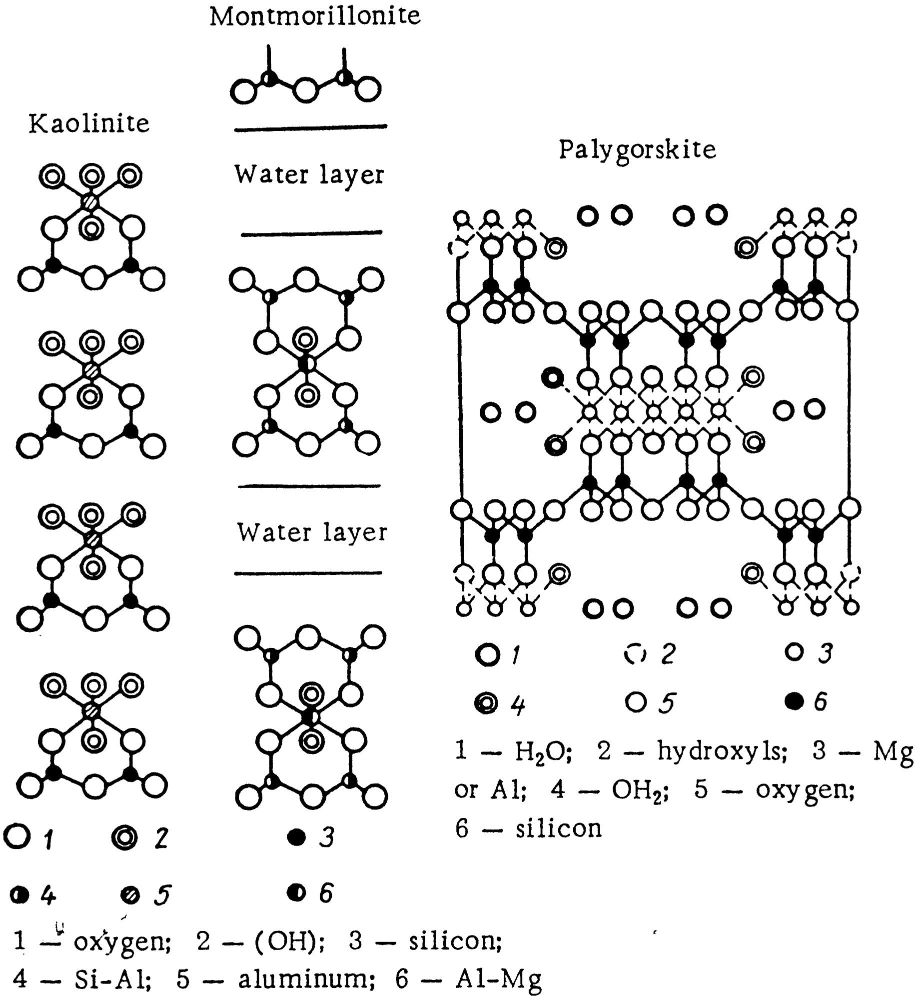


Figure 1. *Crystal structure of kaolinite and the smectite group, represented by montmorillonite, and of palygorskite [5].*

Saponite

Saponite, present in fairly pure form in moderately large deposits in the Madrid area and one of ENRESA's candidate buffer clays, has a specific surface area of 700 to 800 m^2/g [1,4]. The about 10 Å thick lamellae form stacks with 5-10 lamellae depending on the adsorbed cation. Water molecules are adsorbed in the interlamellar space forming one or two hydrate layers depending on the available space and adsorbed cation. The length and width of the stacks is in the range of 0.01 to 0.5 μm. Data on the specific density given in the literature vary very much, but it is proposed that 2600 kg/m^3 be used as an average value. Figure 2 illustrates the morphology of dispersed saponite particles.

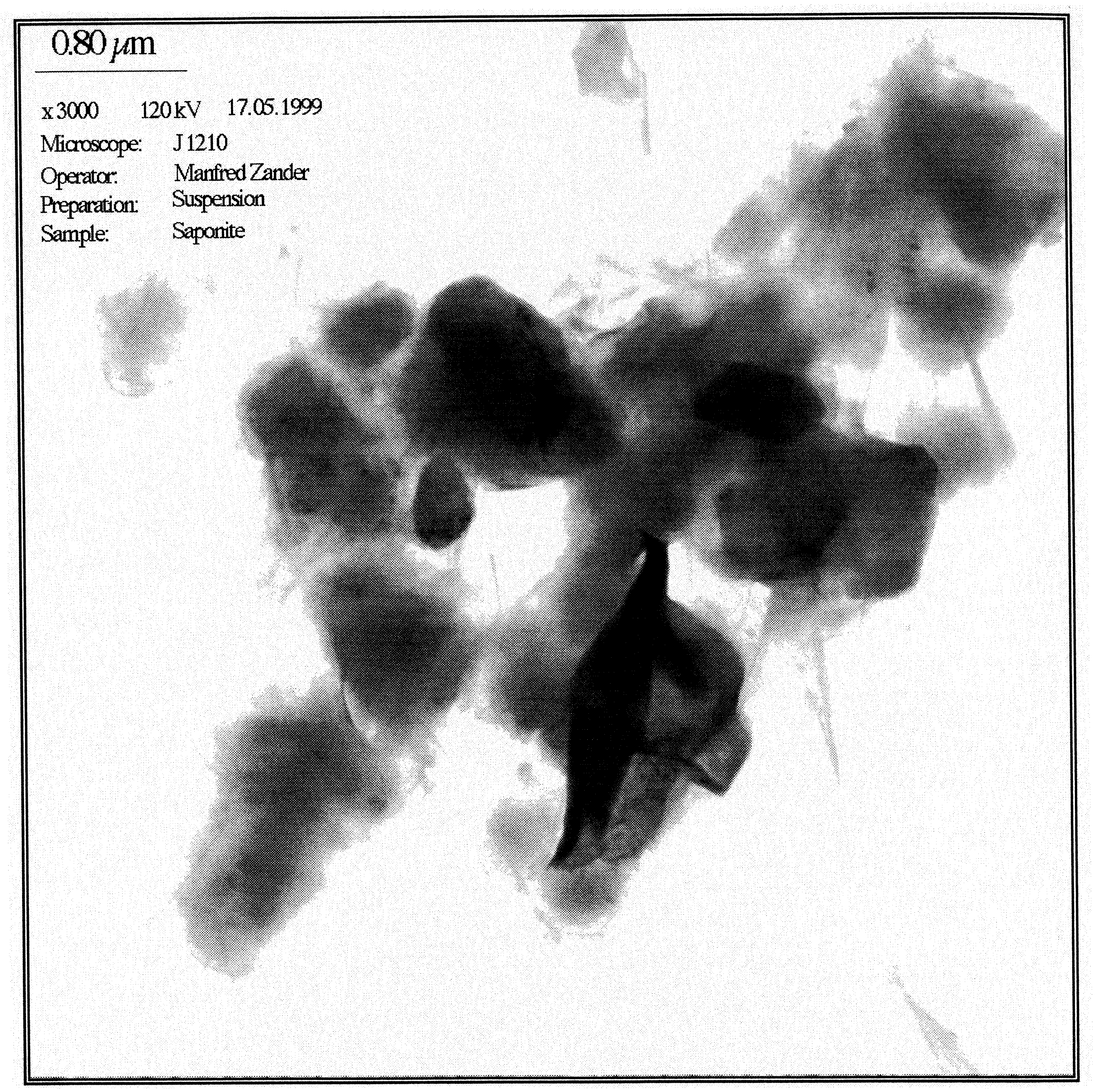


Figure 2. *Transmission electron micrograph of dispersed saponite clay particles. (Photo: J. Kasbohm, Univ. of Greifswald, Germany).*

Mixed-layer minerals

Mixed-layer minerals have a largely varying composition, morphology, grain size distribution and specific surface area. Usually, large deposits of exploitable mixed-layer minerals have a significantly varying composition but the presently investigated deposit has a very uniform composition [2,11]. The specific density can be taken as an average of that of illite and montmorillonite, i.e. 2670 kg/m^3. Figure 3 illustrates the morphology of dispersed particles of mixed-layer smectite/mica, smectite and chlorite, forming major parts of the Friedland clay.

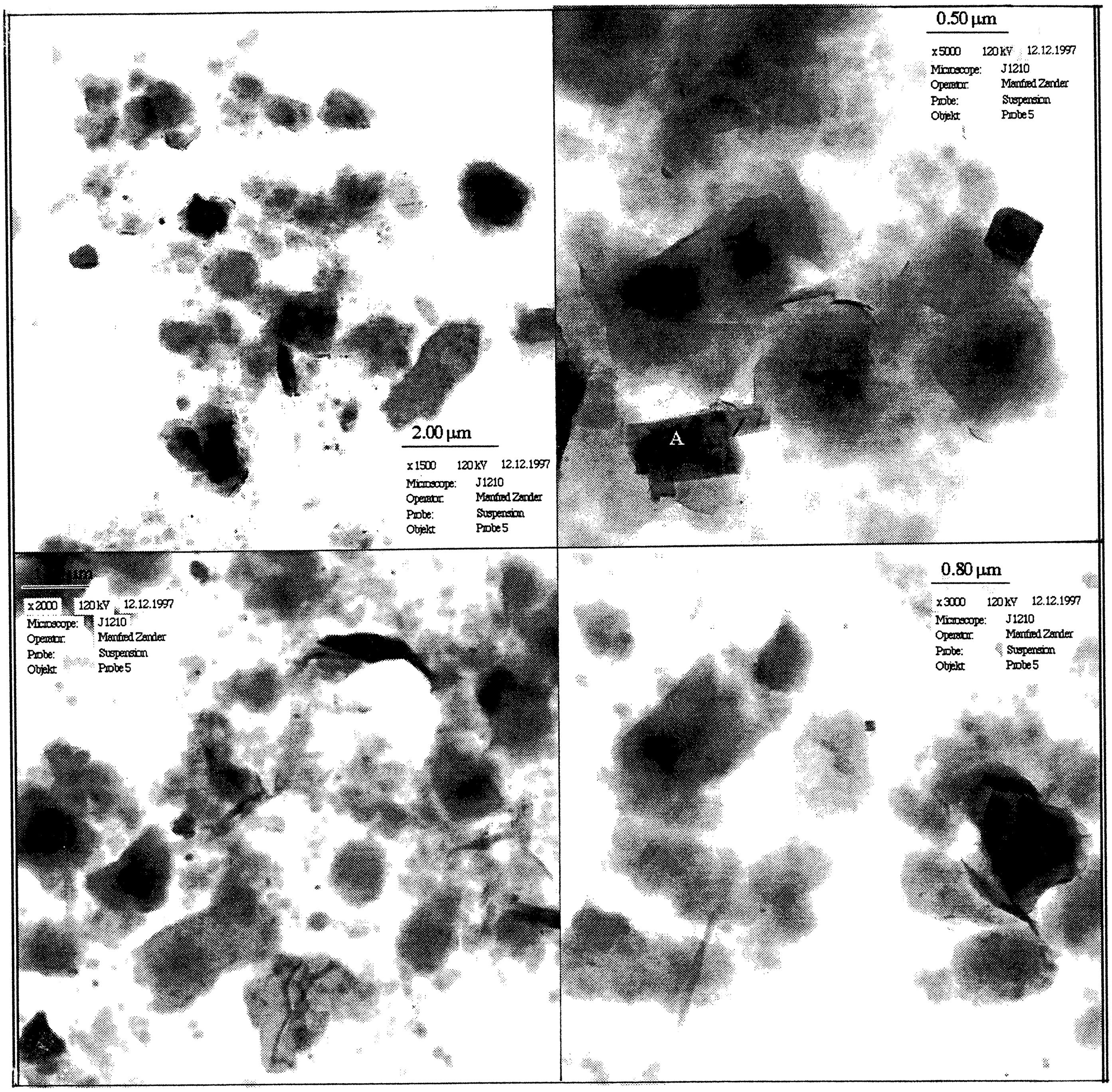


Figure 3. *Transmission electron micrograph of dispersed mixed-layer particles (Friedland clay). (Photo: J. Schomburg, DURTEC, Neubrandenburg, Germany). Small particles with fluffy contours are smectite and mixed-layer crystallites, while most larger ones with distinct contour are chlorite crystals.*

Kaolinite

Kaolinite crystals usually have a distinct pseudohexagonal habit, with aggregates consisting of several, rigidly bound lamellae with 7 Å thickness.

The specific surface area of primary kaolinites is usually 10-50 m^2/g but secondary (altered) kaolinites, like the Glukhov kaolin in the Poloshkovskoe area in Ukraine, are very fine-grained (0.2-0.3 μm) and their specific surface area is up to 200 m^2/g [5]. The specific density varies between 2600 and 2680 kg/m^3 with 2630 kg/m^3 as frequently quoted mean value. Figure 4 illustrates the morphology of the kaolinite investigated in this project.

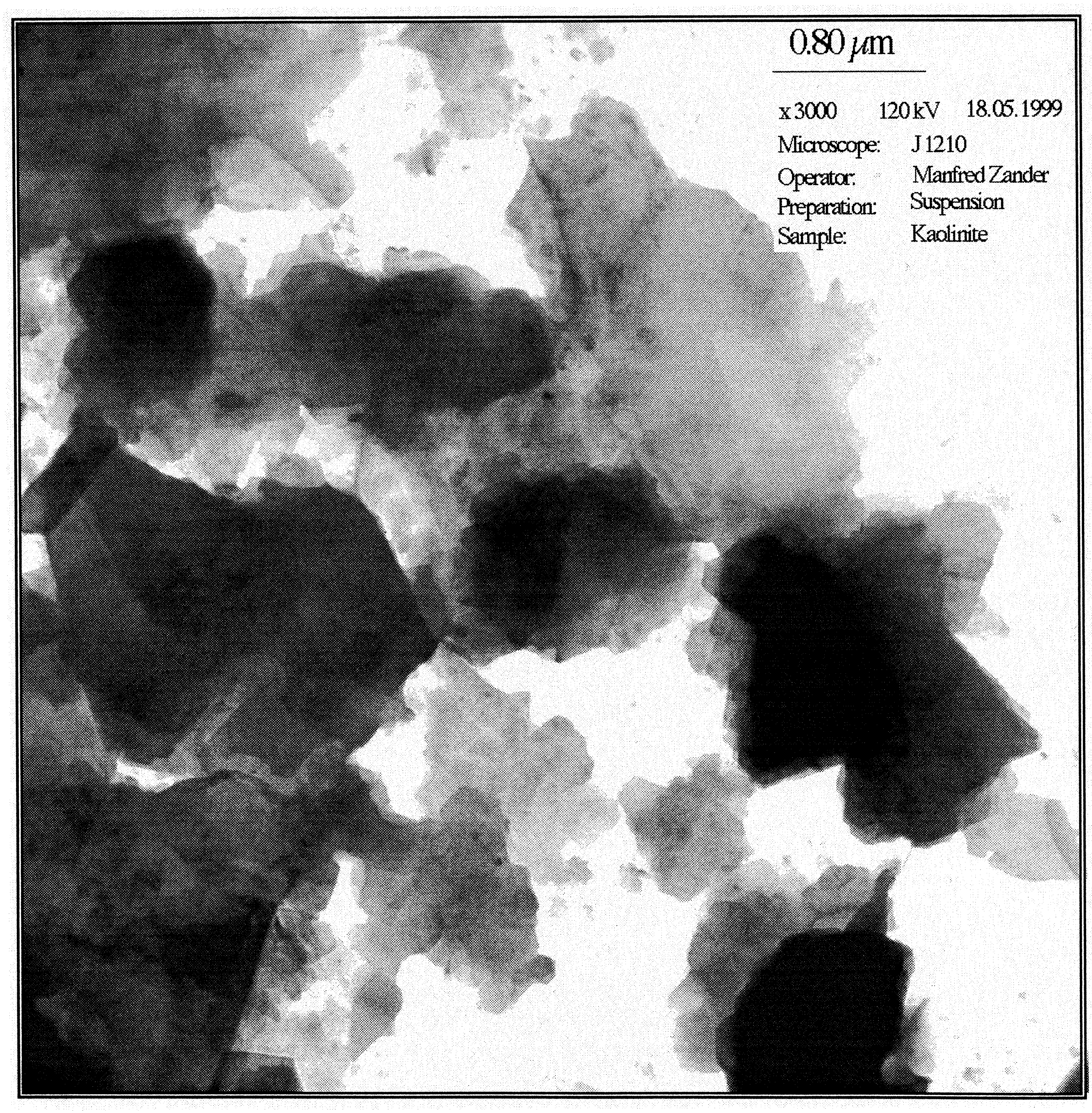


Figure 4. *Transmission electron micrograph of dispersed kaolinite particles (Sachsen). (Photo: J. Kasbohm, Univ. of Greifswald, Germany). The typical big stacks of hexagonal lamellae are major features.*

Palygorskite

Palygorskite has a zeolitic crystal structure, yielding a specific surface area of 900 to 1000 m^2/g [4,5], which is higher than that of the smectites. The length and diameter of the needle-shaped crystals are 0.2-0.8 µm and the width and thickness 100-300 Å, and 50-100 Å, respectively. The channels, which are parallel to the fibers, have a cross section of 3.7 Åx6.4 Å and hence let water molecules through with difficulty. The specific density varies between 2290 and 2360 kg/m^3 an approximate average value being 2330 kg/m^3. Figure 5 illustrates the morphology of palygorskite particles of the presently investigated Greek clay.

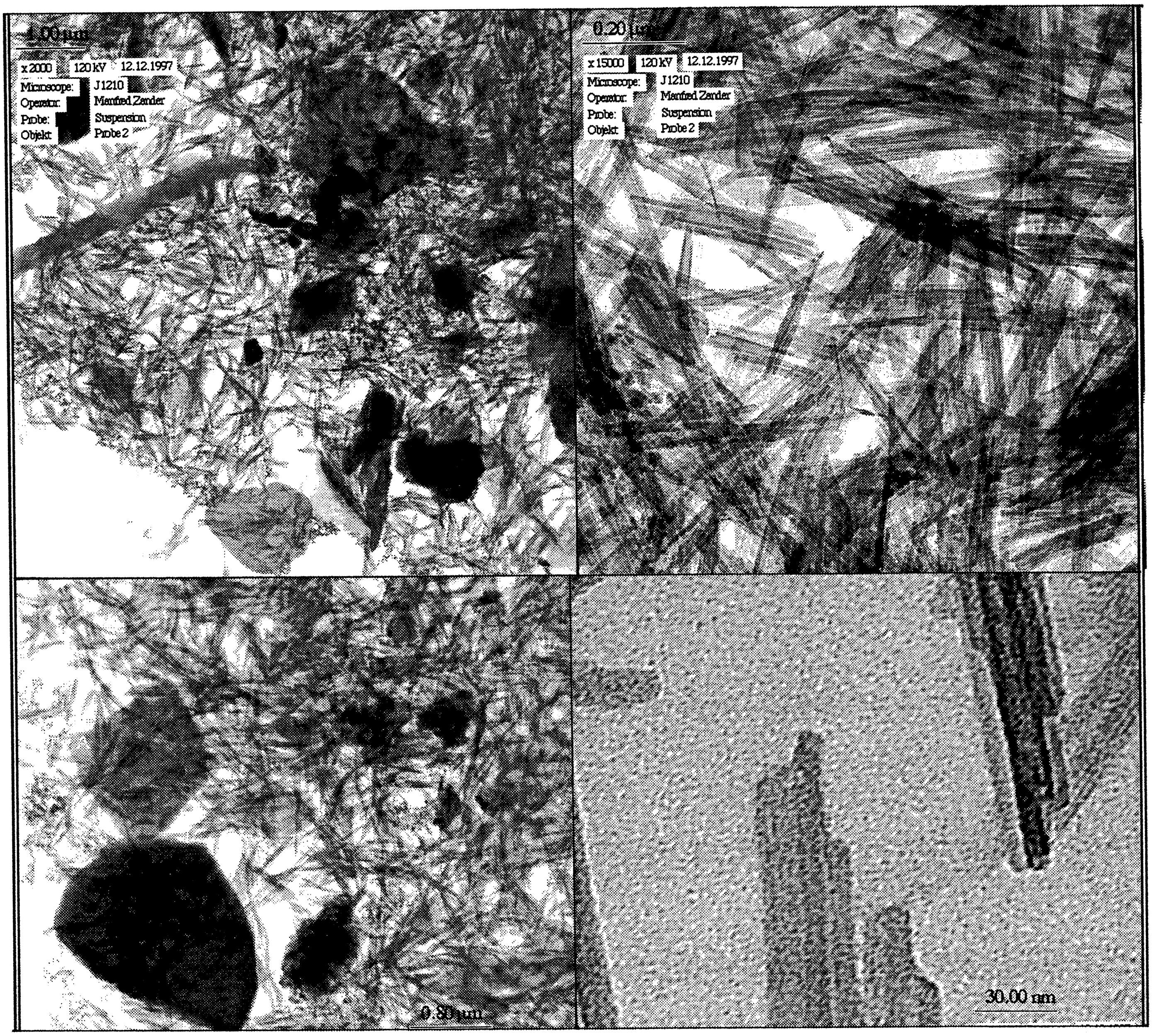


Figure 5. *Transmission electron micrograph of dispersed palygorskite particles (Greece). (Photo: J. Schomburg, DURTEC, Neubrandenburg, Germany).The lath-shape and asbestos-like aggregation are typical. Big opaque minerals are predominantly chlorite and mica crystals.*

Montmorillonite

Montmorillonite, which has the typical smectite nature of stack-forming lamellae, has a specific surface area of about 800 m^2/g [12,13]. The about 10 Å thick lamellae form stacks with 5-10 lamellae depending on the adsorbed cation. Water molecules are adsorbed in the interlamellar space forming up to three hydrate layers depending on the available space and adsorbed cation. The length and width of the stacks is in the range of 0.01 to 0.5 µm. Data on the specific density given in the literature vary very much, but it is proposed that 2700 kg/m^3 be used as an average value. Figure 6 illustrates the morphology of dispersed montmorillonite particles.

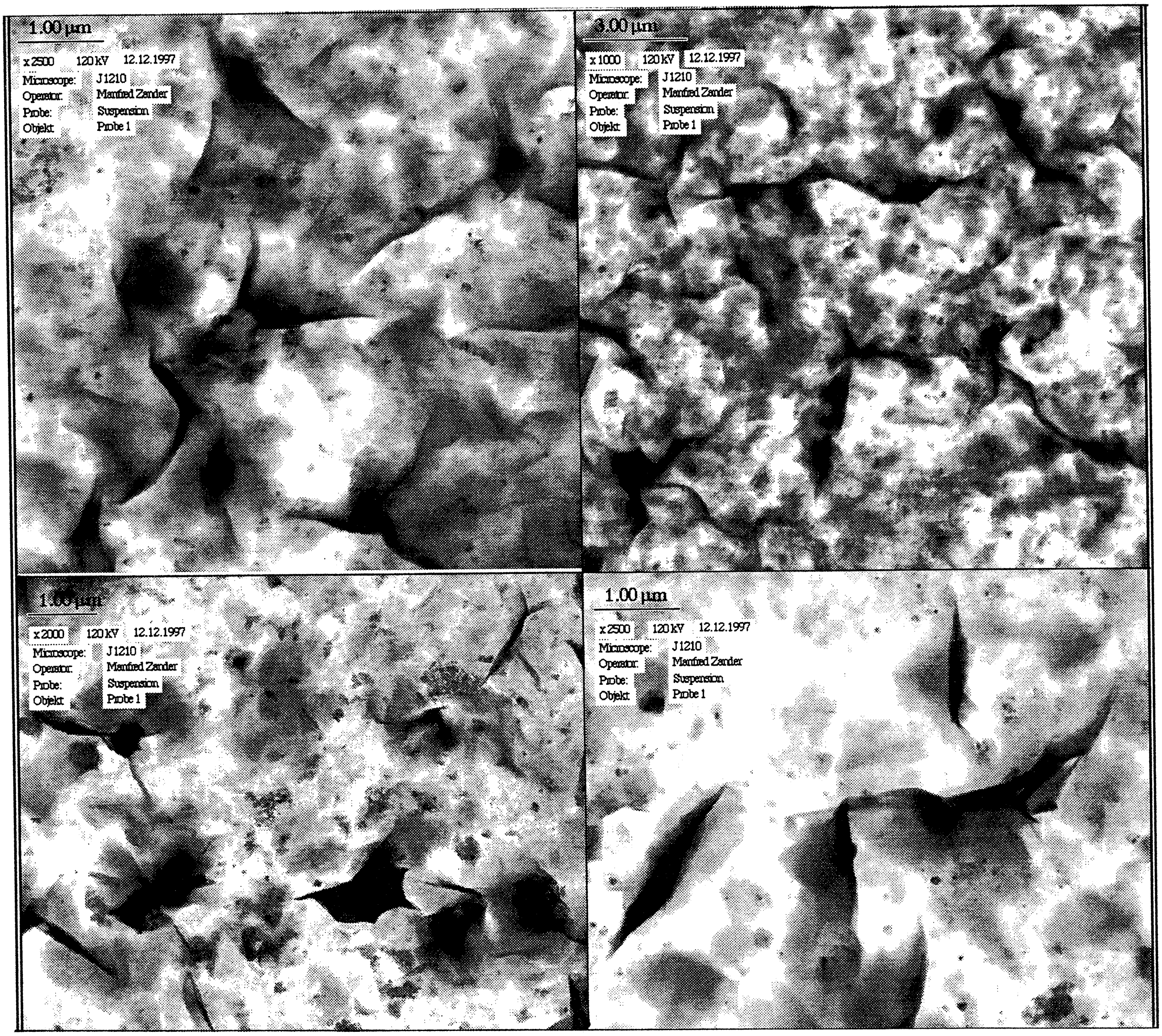


Figure 6. *Transmission electron micrograph of dispersed montmorillonite (MX-80) clay particles. (Photo: J. Kasbohm, Univ. of Greifswald, Germany). The fluffy contours of smaller particles is typical as well as the bat-like appearance of twisted large stacks of lamellae.*

3.4 Chemical composition

3.4.1 Formulae

The following generalized theoretical formula have been proposed for the presently discussed clay minerals excluding sorbed water:

Saponite: $Si_{8-x}Al_x\,Mg_4O_{20}\,(OH)_4$

Mixed-layer (Friedland): $Si_{7.26}Al_{2.96}\,Mg_{0.78}\,Fe_{1.28}\,O_{20}\,(OH)_4$

Kaolinite: $Si_4Al_4O_{10}\,(OH)_8$

Palygorskite: $Si_8\,Mg_5\,O_{20}\,(OH_2)$

Montmorillonite: $Si_8Al_{4-x}\,Mg_x\,O_{20}\,(OH)_4$

3.4.2 Elements

Typical chemical compositions of clay minerals of the investigated types are collected in Table 1. The figures represent the elements expressed in weight percent.

Table 1*. Typical chemical composition of the investigated clay types*

Clay	**SiO_2**	**Al_2O_3**	**Fe_3O_3**	**MgO**	**K_2O**	**Na_2O**
Saponite	45-50	9-10	0-2	24-26	-	-
Mixed-layer	50-57	17-20	4-7	2-5	3-7	0-1
Kaolinite	45-55	30-38	0.3-2	0-0.5	0.3-1.5	0-0.5
Palygorskite	45-55	10-14	1-2	5-9	-	-
Montmorillonite	50-57	15-20	0-6	2-4	0-0.6	0-3

The silica content is similar for all the minerals. The content of aluminum is highest for the kaolinite, montmorillonite and mixed-layer smectite-mica clay. Magnesium is abundant in saponite and the content of this element is relatively high also for palygorskite. The compositions of chloritic mixed-layer smectite-mica clay of the presently discussed type and of typical montmorillonite clay are very similar, except that the former has significantly more potassium. It is firmly held in the interlayered mica and the associate mineral chlorite.

4 PHYSICAL PROPERTIES

4.1 General

The isolation potential of buffer clay is primarily determined by its hydraulic conductivity and ion diffusion transport capacity. The first property depends on the microstructural homogeneity, which is controlled by the gel forming and swelling potentials. The other depends on the sorption potential, which is a function of the ion exchange capacity. Thermal and rheological properties are important as well since they determine the heat conditions and stress/strain behavior of the buffer.

4.2 Hydration

Saponite

The 10 Å saponite lamellae, which consist of two silica tetrahedral sheets with a central alumina octahedral sheet, form stacks with a number of lamellae per stack that is estimated to be similar to that of other smectite minerals. No more than two interlamellar hydrate layers can be established in saponite with Na as adsorbed cation, and only one for K and Ca [14]. The hydration potential is indicated by the fact that the water content at RH=100 % is about 15 %.

Mixed-layer smectite-mica

Mixed-layer smectite-illite has been reported to have little tendency to form thick stacks [4]. This suggests that there is not much interlamellar "internal" water and that "osmotic" water, adsorbed on the outer surfaces of the thin stacks, and free water occupying the large majority of the voids, dominate. The swelling capacity is consequently rather small, i.e. 45 % expansion of clay saturated with distilled water to a bulk density of 2000 kg/m^3 before expansion, compared to more than 180 % of MX-80 with 75 % montmorillonite [11]. Air-dry mixed-layer clay powder that contains about 45 % smectite has a water content of about 10 % when stored in RH=100 % atmosphere [11].

Kaolinite

The 7 Å lamellae, consisting of a single silica tetrahedral and a single alumina/ octahedral sheet, are held together rather strongly by hydrogen bonds. The book-like stacking gives a small specific area which explains its poor hydrophilic character. This is because water molecules are bound to the crystals only by hydrogen bonds between hydroxyls and oxygens exposed at the edges. Fine grinding of kaolinite significantly increases the hydration potential because the specific surface area is then appreciably increased [4]. Air-dry clay powder with 75 % kaolinite has a water content of about 7 % when stored in RH=100 % atmosphere.

Palygorskite

The crystal structure of palygorskite precludes intracrystalline swelling. In contrast to smectites, lattice substitutions and lattice charge of palygorskite are insignificant, and hydration takes place by hydrogen bonding between water molecules and hydroxyls and oxygens in the intracrystalline channels (Figure 7). Heating palygorskite to 120°C displays endothermal effects due to loss of adsorbed water, and heating to 180°C causes an increase in heat of wetting due to loss of the most strongly bound water in the channels. While hydration of smectite is largely controlled by the exchangeable cations, wetting of kaolinite and palygorskite is due to hydrogen bonds established between water molecules and the crystal surfaces.

Four water molecules are present in the channel per unit cell and four others are bound to octahedral cations. On heating, these latter molecules are lost in 2 stages: two of them are released first by which the structure collapses by fiber rotation yielding folding. Heating to 150°C removes 10 % of the zeolitic water and complete dewatering takes place at 600°C at which temperature the channels become closed. The sorption of water at normal temperature is very high due to the zeolitic structure and palygorskite can retain up to 250 % of its mass. It has been reported to have 50 % more hygroscopic moisture than montmorillonite [5].

Expansion by uptake of polar molecules takes place and this is assumed to be associated with reversible structural rearrangement approaching the state of plane sheet phyllosilicates. It may even take the form of conversion from palygorskite to montmorillonite. The close relationship between the two minerals is demonstrated by the fact that they often form neighboring or interfingered deposits as in Ukraine. The swelling of palygorskite has been reported to be almost the same as for Na montmorillonite [5].

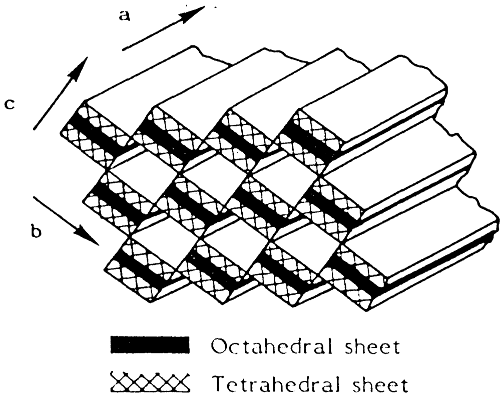
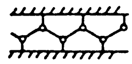
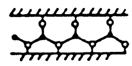
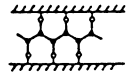
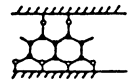
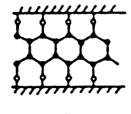
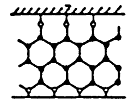
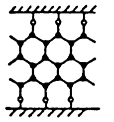


***Figure** 7. Palygorskite structure lying on (011).*

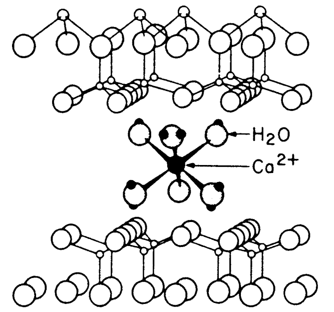
Montmorillonite

The 10 Å montmorillonite lamellae, which consist of two silica tetrahedral sheets with a central alumina/magnesium octahedral sheet, form stacks with 3-5 lamellae per stack when Na is adsorbed and 5-10 when Ca is in interlamellar positions. Up to three interlamellar hydrate layers can be established in montmorillonite with Na as adsorbed cation, and two for K and Ca [14]. The strong hydration potential is indicated by the fact that the water content at RH=100 % is about 20 %.

The general nature of the hydration process and organization of interlamellar water are indicated in Figure 8. It illustrates the model of Forslind and Jacobsson of a regular water lattice being formed when Li or Na are in interlamellar positions [15], and a model assumed to be valid when Ca ions are in these positions. In the latter case the hydration of the cations is too strong to allow an independent water lattice to be established.

	Schematic interlayer structure	H_2O molecules per unit cell	Basal spacing, Å	g H_2O/g clay	mM H_2O/g clay	Remarks
0		0	12.30	0; 0,084*	0; 4.667*	Unstable; no hydration; four OH groups per unit cell
1		2.66	15.05	0.059	3.278	Unstable
2		5.33	17.81	0.119	6.661	Stable monolayer
3		8.0	18.73	0.179	9.944	Unstable
4		10.67	21.49	0.238	13.222	Stable; two layers
5		13.32	22.41	0.297	16.5	Unstable
6		16.0	25.17	0.357	19.833	Stable; three layers

* At complete dehydroxylation.



OUTER-SPHERE SURFACE COMPLEX: $Ca(H_2O)_6^{2+}$ ON MONTMORILLONITE

***Figure 8**. Hydration of montmorillonite. Left: Forslind's model for Li and Na states. Right: Ca-water bonding forming outer-sphere surface complexes [16].*

4.3 Transport properties

4.3.1 General

The practically important properties of buffers that control the transport properties are the water permeability, the critical gas pressure, and the diffusive ion transport capacity. They are all controlled by the microstructure, which is hence taken as a basis of the issues.

4.3.2 Hydraulic conductivity

The continuity of the system of voids is the most important factor for the bulk hydraulic conductivity. It is strongly dependent on the hydration potential of the clay minerals, which determines the expandability, and on their gel-forming ability.

The size distribution and continuity of voids and high-permeable paths in the matured clay depend strongly on the bulk density, porewater chemistry and type of clay, i.a. because of the different potential of the powder grains to exfoliate and give off clay aggregates that can rearrange and establish continuous clay gels [7,17]. The following general description is based on a detailed study of montmorillonite, which has been adapted to the other clay types.

Saponite

Saponite expands less than montmorillonite and therefore has less ability to seal the voids formed between the powder grains that are compressed to yield the buffer material. For moderate densities, low porewater electrolyte contents the difference between montmorillonite and saponite in void size and interconnectivity and therefore also in hydraulic conductivity should be less obvious than at high porewater salinity. For high densities the importance of the salinity is not expected to have a significant impact on the hydraulic conductivity because the sealing effect of clay particle gels in larger voids is less important when the voids are small.

A schematic section of the microstructure of an element of saponite clay with 100 % expandable particles, representing a bulk density of about 2000 kg/m^3, would be as shown in Figure 9. It illustrates orthogonally grouped stacks (A) of lamellae. Wide, empty voids (B), and small empty voids (C) combine to form tortuous, more or less continuous paths with cross sections varying between 0.1 and 5 μm. The stacks of lamellae contain only immobile water, while continuous voids let water through. The permeable fraction of a cross section of at least 30 μm x 30 μm, is about 10-20 % [18].

The difference in microstructural geometry in Na- and Ca-saturated saponite with this density is expected to be small and the hydraulic conductivity is hence not believed to be very different. Local, isolated voids with no particles in may be up to 10-15 µm but they do hardly contribute to the net hydraulic conductivity.

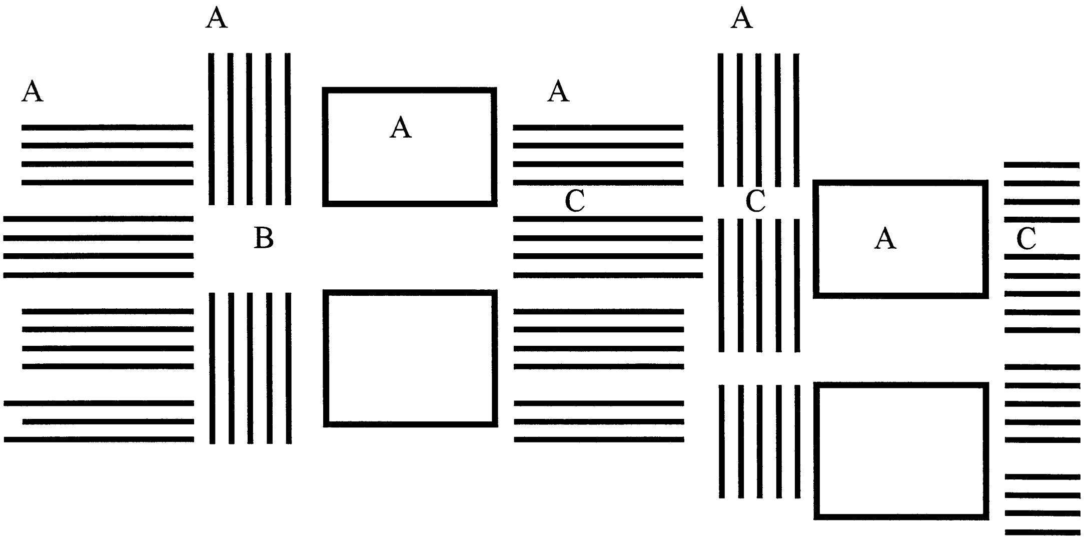


Figure 9. Schematic microstructural model of dense saponite clay with orthogonally grouped stacks of lamellae. A) Impermeable stacks of 10 Å lamellae separated by 1-2 hydrate layers. B) Open, very permeable, large void. C) Permeable, narrow void.

Mixed-layer smectite-mica

Mixed-layer clays with smectite associated with non-expanding minerals swells according to the smectite content. They have less ability to seal the voids formed between the powder grains than saponite and at high porewater electrolyte contents and low bulk densities the hydraulic conductivity can be on the same order of magnitude as has been recorded for non-expandable illite or illite/chlorite clay. At densities typical of buffer material and low-electrolyte porewater, the hydraulic conductivity may be about one order of magnitude higher than that of saponite.

Using the same schematic section of the microstructure of an element of saponite clay but with about 50 % non-expandable particles, one would get the picture in Figure 10 for a bulk density of about 2000 kg/m^3. It illustrates expandable smectite/mica stacks of lamellae (A). Wide (B) and small (C) voids form paths with cross sections varying between 0.1 and 10 µm. The fact that a smaller part of the porewater is immobile and that more voids form contionuous paths mean that the hydraulic conductivity is substantially higher than for saponite clay with the same density. The permeable fraction of a cross section of at least 30 µm x 30 µm, is estimated to be about 15-25 %.

The difference in microstructural geometry in Na- and Ca-saturated mixed-layer clay of this sort and with this density is larger than in the saponite case because the gels in the voids will coagulate on Ca-saturation and this should imply a somewhat higher hydraulic conductivity in the Ca case. Local, isolated voids with no particles in may be up to 25 μm but they do hardly contribute significantly to the net hydraulic conductivity.

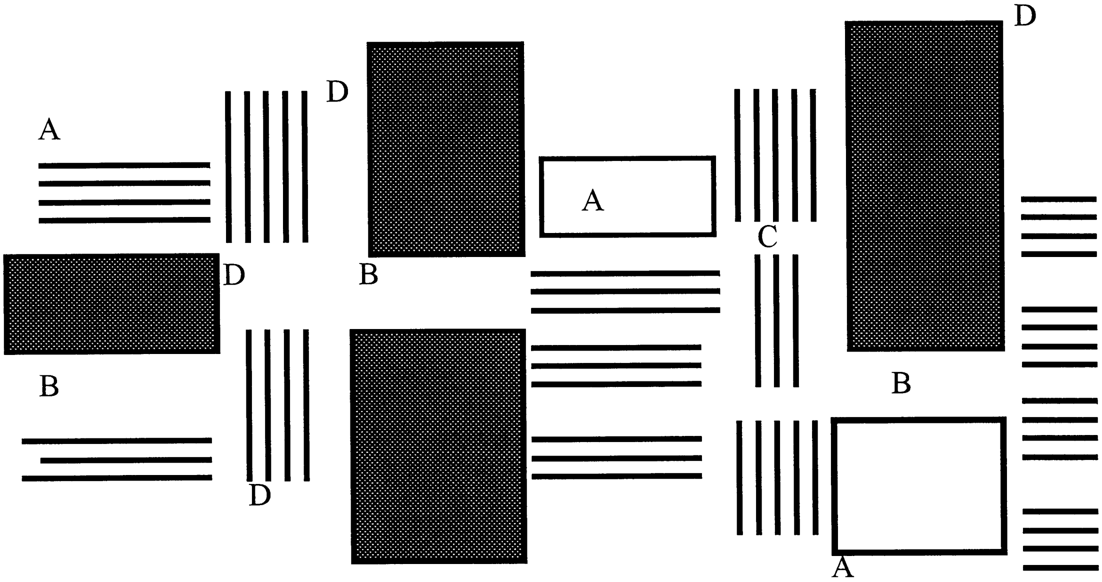


__Figure 10.__ Schematic microstructural model of dense mixed-layer smectite-mica clay. A) Impermeable stacks of 10 Å lamellae separated by 1-2 hydrate layers. B) Open large void with soft smectite gel. C) Permeable narrow void. D) Mica or chlorite grain (black).

Figure 10 serves to illustrate the limited expandability, which gives less good homogeneity of this type of clay than of smectites like saponite. An important advantage in using smectitic mixed-layer minerals instead of artificial mixtures of ballast and expandables is that all grains contain some expandables, which form clay gels in voids between larger grains.

Kaolinite

Pure kaolinite has a very small expansion capacity. At densities typical of buffer the hydraulic conductivity may be more than two orders of magnitude higher than that of saponite at any porewater chemistry.

Using the same microstructural section as previously but taking the stacks of lamellae to be thicker and not expandable, one would get the picture in Figure 11 for a bulk density of 2000 kg/m^3 at saturation. It illustrates orthogonally grouped kaolinite stacks (A) of lamellae. Wide voids (B) and small voids (C) form continuous paths with cross sections varying between 0.2 and 20 μm. The fact that all the porewater is mobile and that all the voids form continuous paths means that the hydraulic conductivity is substantially higher than for saponite and mixed-layer smectite-mica clay with the same density. The permeable fraction of a cross section of at least 30 μm x 30 μm, is estimated to be about 25-35 %.

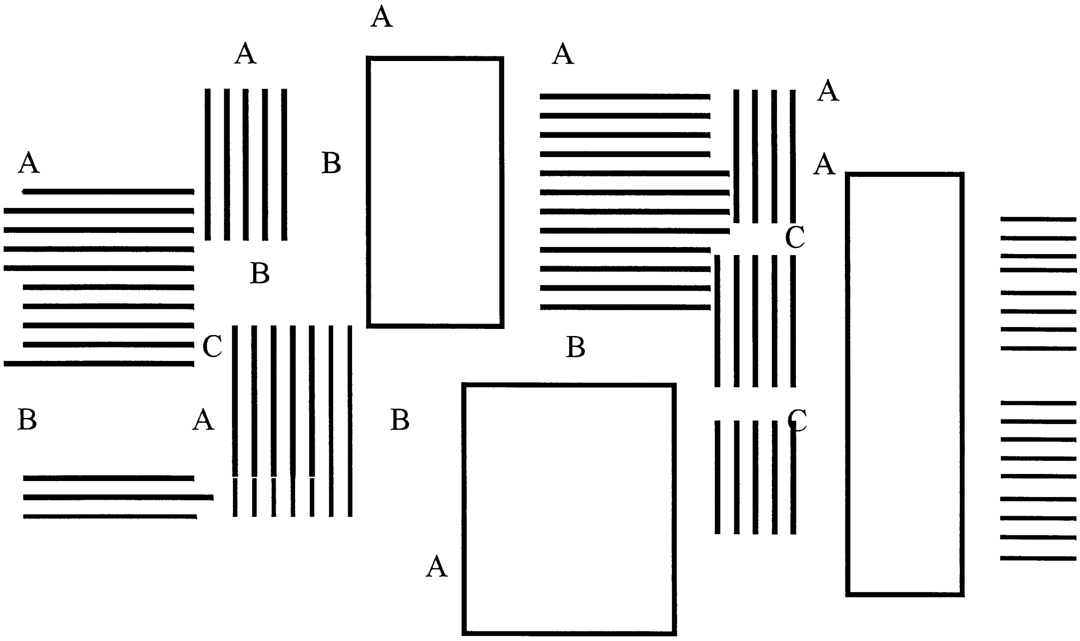


***Figure 11**. Schematic microstructural model of dense kaolinite clay with orthogonally grouped stacks of 7 Å lamellae. A) Coherent, impermeable stacks of 7 Å lamellae. B) Open large void. C) Narrow void.*

Palygorskite

Palygorskite may expand as much as pure smectites but is expected to have less ability to seal the voids formed between the powder grains that are compressed to yield the buffer material. In contrast to saponite and montmorillonite the influence of porewater chemistry on the microstructure of palygorskite clay and hence on its hydraulic conductivity should be insignificant according to the hydration mechanisms described earlier.

The microstructure of an element of palygorskite clay is very different from that of smectites, mixed-layer clays and kaolinite. Figure 12 illustrates very schematically the arrangement of fibrous particles at a bulk density of about 2000 kg/m^3. The particles are orthogonally grouped stacks (A) of fibers. A large number of them break, bend and twist at the compaction under high pressure, which means that the large majority of the voids become small (C). They combine to form tortuous, more or less continuous paths with cross sections varying between 0.1 and 5 μm. The fibers contain water but are not very permeable because their channels are very narrow. The permeable fraction of a cross section of at least 30 μm x 30 μm, is estimated at 10-20 % at a bulk density of 2000 kg/m^3.

Like in kaolinite all the porewater is mobile and all the voids form continuous paths. However, since the channel water is expected to have limited fluidity the hydraulic conductivity should be lower than for kaolinite. Still, it is expected to exceed that of saponite.

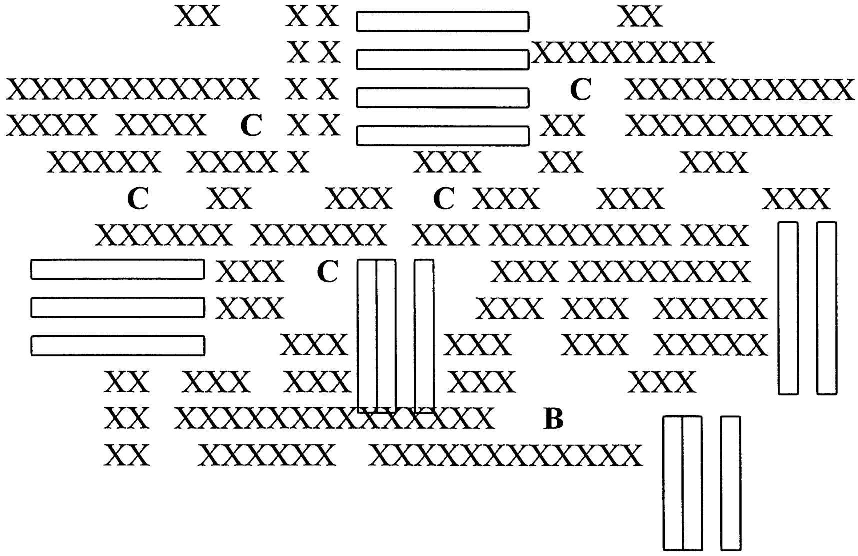


Figure 12. *Schematic microstructural model of palygorskite with orthogonally grouped fibers. X-sets and rectangels are bunches of fibers.* ***B)*** *Large void. C) Permeable narrow void.*

Montmorillonite

Montmorillonite has the strongest ability to expand and form gels of all clay minerals and therefore a high potential to seal the voids formed between the powder grains that are compressed to yield the buffer material. For low porewater electrolyte contents the difference in void size and interconnectivity between montmorillonite and saponite and therefore in hydraulic conductivity is small at high densities while it can be appreciable at low densities.

A schematic section of the microstructure of an element of montmorillonite clay with 100 % expandable particles, representing a bulk density of about 2000 kg/m^3, would be as shown in Figure 13 [18]. It illustrates orthogonally grouped stacks (A) of lamellae. Wide voids (B), largely filled with clay gel formed by montmorillonite particles exfoliated from dense parts in the saturation process and rearranged in the voids, and small empty voids (C) combine to form tortuous, more or less continuous paths with cross sections varying between 0.1 and 5 μm. The stacks of lamellae contain only immobile water, while continuous voids let water through. The permeable fraction of a cross section of at least 30 μm x 30 μm, is about 10-20 % [18]. These parts represent clay gels with a density of 1200 to 2000 kg/m^3 for bulk clay densities ranging between 1600 and 2100 kg/m^3.

The difference in microstructural geometry in Na- and Ca-saturated montmorillonite of high density is small and the difference in bulk hydraulic conductivity is hence not believed to be significant. Local, isolated voids with no particles in may be up to 3-5 μm wide but they do hardly contribute to the net hydraulic conductivity.

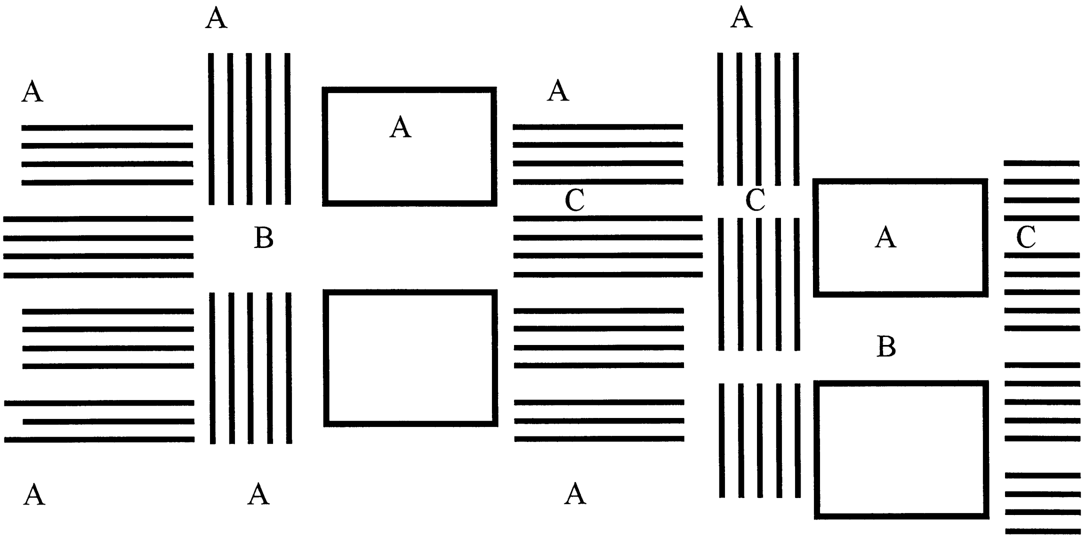


Figure 13. Schematic microstructural model of dense montmorillonite clay with orthogonally grouped stacks of lamellae. A) Impermeable stacks of 10 Å lamellae separated by 1-2 hydrate layers. B) Gel-filled very permeable large void. C) Gel-filled poorly permeable narrow void [18].

Referring to the microstructural constitution of the considered clay types (Figures 9 to13) one would expect the following ranking with respect to the hydraulic conductivity, assuming the bulk density at water saturation to be about 2000 kg/m^3 and considering the most conservative case, i.e. that with salt porewater with Ca as dominant cation:

1. Montmorillonite clay is believed to have the lowest hydraulic conductivity since the gel fillings in the voids have a rather high density and homogeneity. Ordinary conductivity data should be in the range of E-14 to E-13 m/s using recent microstructural models [18].

2. Saponite clay has the second lowest conductivity, still being on the same order of magnitude as montmorillonite when Na is the dominant cation, but somewhat higher when Ca dominates. The average hydraulic conductivity is hence expected to be on the order of E-13 m/s.

3. Mixed-layer smectite-mica clay is expected to have the third lowest conductivity because there should be some degree of gel-filling of the voids as indicated by the microstructural model. Estimates based on micro-

structural analyses using transmission electron microscopy [18] yield an expected average hydraulic conductivity at the density 2000 kg/m^3 of around E-11 m/s.

4. Palygorskite is assumed to have the second highest conductivity since there is no void-filling, expansive component. However, since the major conductivity-reducing factors, i.e. the tortuosity of the flow paths and the very low permability of the fiber channels have not been quantified, the bulk conductivity may be lower than assumed here. No conductivity data are given in the literature.

5. Kaolinite should have the highest conductivity because of the absence of expandable, void-filling components and because of the relatively large grain size if very effective grinding is not applied. Probable conductivity data should correspond to those of very fine-grained quartz/feldspar silt soils, which are in the range of E-10 to E-8 m/s.

Since a too high hydraulic conductivity means that a major criterion for the buffer function is not fulfilled, it may be that only four candidates qualify, i.e. clays with montmorillonite, saponite, mixed-layer smectite-mica, and palygorskite as major minerals. MX-80 has the highest rank.

4.3.3 Critical gas pressure

Gas penetrates clays in a finger-like mode when the gas pressure exceeds the sum of the piezometric head and and a critical (threshold) pressure, which has been experimentally validated [19,20]. The microstructural heterogeneity explains why pressurized gas moves in local pathways. They are ”paths of least resistance” represented by interconnected voids or elements that are empty or filled with clay gels with lower density than the rest of the clay matrix.

For dense smectite clay of montmorillonite-type, the critical pressure is logically related to its swelling pressure since gas penetration requires separation of dense matrix components (”fracturing”). This has been aptly demonstrated by experiments with MX-80 [19], which have shown that the critical gas pressure may be as high as the swelling pressure for this sort of clay when the bulk density is higher than about 1500 kg/m^3. For a bulk density at complete water saturation of around 2000 kg/m^3, the critical gas pressure may be on the order of 5-10 MPa. Gas pressure tests have also been made on clays with illite and chlorite as major clay minerals and with 10-20 % smectite and they validate the relationship between the critical and swelling pressures. For these clays the critical gas pressure was found to be appreciably lower than that of MX-80, which is easily understood by considering the difference in microstructure as illustrated by Figures 10 and 13. Thus, the large number of incompletely gel-sealed voids between non-expandable grains in the smectite-poor clay offers less resistance to gas penetration than the dense montmorillonite clay, and let gas through at lower pressure.

Referring to the microstructural constitution of the considered clay types (Figures 9-13) one would expect the following ranking with respect to the critical gas pressure, assuming the bulk density at water saturation to be about 2000 kg/m^3:

1. Montmorillonite clay should have the highest critical pressure, i.e. 5-10 MPa. Gas penetration implies microstructural changes.
2. Saponite clay should have the second highest critical pressure, but still on the same order of magnitude as montmorillonite at least when Na is the dominant cation. Gas penetration probably implies microstructural changes.
3. Mixed-layer smectite-mica clay is expected to have the third highest critical pressure, probably around 1 MPa. Gas penetration may imply some microstructural changes.
4. Palygorskite is believed to have the second lowest critical pressure, probably corresponding to the capillary pressure. Since the estimated void size is in the range of 0.1-5 μm and the average size 1 μm, the capillary pressure would be on the order of 200-500 kPa [19].
5. Kaolinite logically has the lowest critical pressure; it is expected to correspond to the capillary pressure. Since the probable void size is in the range of 0.2-20 μm and the average size 2 μm, the capillary pressure would be less than 200 kPa [19].

Since high critical pressures may imply overstressing of the canisters, scoring with respect to gas pressurization would imply that kaolinite is preferable while MX-80 is the least attractive candidate. Mixed-layer smectite-mica and palygorskite are expected to be almost as good as kaolinite, while saponite, has the same ranking as montmorillonite.

4.3.4 Sorption

The ion sorption ability, which is related to the ion exchange capacity of the buffer, is primarily of importance for the ion diffusion capacity, which is discussed in Section 4.3.6.

Saponite

The sorption sites on saponite minerals are in the interlamellar space for balancing charge deficits in the octahedral layers, on the basal surfaces for balancing the overall negative charge of the crystals, and on the edges (OH groups). pH has the impact on edge charges that is indicated in Figure 14. Thus, at low pH, the stack edges carry positive charge and adsorb anions, while at high pH the edges become negatively charged and adsorb cations. At intermediate pH, the charge may be low, negative or positive, depending on the geometry and nature of the stacks.

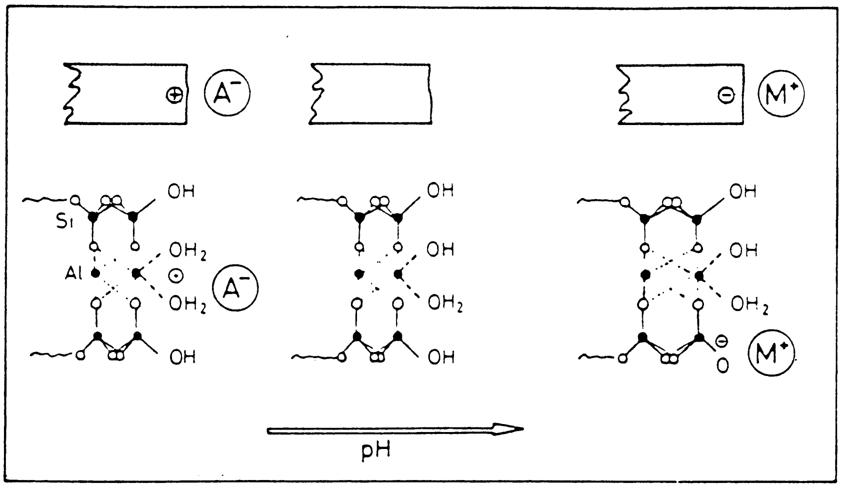


Figure 14. Influence of porewater pH on the edge charge of phyllosilicates [17].

Mixed-layer smectite-illite

The sorption sites are in the interlamellar space of the smectite-mica component for balancing charge deficits in the octahedral layers, on the basal surfaces for balancing the overall negative charge of the crystals, and on the edges (OH groups). The sorption sites of the micaceous component are solely the edge-exposed OH groups and it has been demonstrated that metal adsorption causes deprotonation and forms surface complexes [4]. The dominant sorption sites of the chlorite component are on the basal surfaces and to a smaller extent on the edges (OH groups). pH controls the sorption potential of the stack edges. The total cation sorption should be about 50 % of that of saponite because of the lower smactite content.

Kaolinite

The sorption sites are on the edges (OH groups). pH controls the sorption potential of the stack edges. The sorption capacity is very small except if the clay is very fine-grained.

Palygorskite

The palygorskite structure has three sorption centers:

1. Oxygens in the tetrahedral ribbon sheets
2. Water molecules (two for each Mg ion) coordinated to magnesium
3. SiOH groups along the fiber axis (5 Å spacing)

The silanol groups are formed by uptake of protons or hydroxyls by broken Si-O-Si at external surfaces. The groups are active sorption sites that interact with molecules like water and organic molecules as well as exchangeable cations, which can hydrate.

Montmorillonite

Montmorillonite is comparable to saponite.

4.3.5 Ion exchange

Cation exchange

Saponite

Like most smectites, saponite exhibits a high cation exchange capacity. It has been found to be 80-110 meq/100 g [4,7].

Mixed-layer smectite-mica

The major cation-exchanging part of the presently considered mixed-layer smectite-mica clay is the smectite while the mica provides has a low exchange capacity. Since smectite with 100 meq/100 g CEC makes up 50 % of the expandables, i.e. 25 % of the total mineral mass, one would expect a net CEC of about 25 meq/100 g. Experimental values for the mixed-layer clay in focus of the present study (Friedland clay) are higher, i.e. 60 meq/100 g as an average [2], the reason being that the clay contains about 20-30 % chlorite and mica which also contribute to the cation exchange capacity.

Kaolinite

The cation exchange capacity of kaolinite strongly depends on the size of the crystals since it determines the edge surface area. Hence, for 1-2 μm size it is 8-10 meq/100 g, while it can be 70-100 meq/100 g after intense grinding [4,7].

Palygorskite

The literature contains several indications of a limited frequency of crystal lattice defects causing charge deficiencies in palygorskite and this would mean that the cation exchange capacity should be rather low. Typical reported data are in agreement with this; they are in the interval 29-35 meq/100 g, i.e. about 30 to 40 % of that of montmorillonite [5,6].

Montmorillonite

Montmorillonite has a cation exchange capacity of 80-110 meq/100 g [4,7].

Anion exchange

Saponite, mixed-layer smectite/illite, and montmorillonite should all have a low anion exchange capacity because the edge surface area, which provides sites for such exchange under certain conditions, is small. Accordingly, the anion exchange capacity (AEC) has been reported to be lower than 5-7 meq/100 g [4,7]. The exchange mechanism is thought to be replacement of OH-groups by other anions, which implies that clay minerals with a large number of OH:s exposed on the surfaces, like kaolinite and palygorskite may have an appreciable AEC. For these two minerals AEC is in fact only slightly lower than CEC. Thus, for palygorskite AEC is around 20-25 meq/100 g and for very fine-grained kaolinite it may be 50-90 meq/100 g [4]. It can be assumed that finely ground palygorskite may have a similar anion exchange capacity.

High sorption and ion exchange capacities mean that ion diffusion through the buffer is retarded. It is concluded that montmorillonite and saponite are more effective cation catchers than kaolinite and palygorskite. Significant anion adsorption is only provided by palygorskite and very finely ground kaolinite.

4.3.6 Ion diffusion

For montmorillonite, the stochastic nature of the microstructure implies that both the width and straightness of high-porous zones vary and that the their gel-fillings have a varying density. Terming the zones channels [18], the channel geometry and gel density vary over any individual cross section in virtually isotropic clay. The fraction of a cross section that represents the most permeable parts also has the highest cation and anion diffusion transport capacity, while the densest parts let only small weakly hydrated cations through but no anions, which are Donnan-excluded. For high bulk densities the ratio of the void volume for diffusive migration of many cations to that of anions should hence be on the order of 10-50 as concluded from microstructural analyses, which is not too different from experimentally determined data. K_d, which is a parameter that affects the cation migration rate and is defined as the ratio of the concentration of solute sorbed on the solid matrix and the concentration in the solution, depends on the size of the mineral surfaces per unit volume and hence on the density. This parameter can be estimated on the basis of quantitative microstructural analyses (10-100 l/kg [18]) and is logically much higher for the smectitic clays than for palygorskite and kaolinite.

Direct comparison of the ion diffusion capacities requires that a specific ion species be considered and that the effective diffusion coefficient D_e is used as parameter [18]. The cation strontium and the anion iodine are referred to here.

Taking strontium and iodine as reference cation and anion, respectively, and referring to the microstructural constitution of the considered clay types (Figures 9-13), one would expect the following ranking with respect to the diffusion capacities assuming the bulk density at water saturation to be about 2000 kg/m^3:

1. Montmorillonite clay is expected to have the lowest D_e for Sr because of the strong sorption in the dominant dense parts. It is also believed to have the lowest D_e for I because of the small volume available for anion migration.
2. Saponite clay should have ion diffusion properties that are similar to those of montmorillonite because of the similar microstructural and mineral constitutions. D_e for the considered ions is expected to be slightly higher than for montmorillonite.
3. Mixed-layer smectite-mica clay should have somewhat higher cation and anion diffusion capacities than smectites because of the larger content of free water. D_e for the considered ions is thus expected to be appreciably higher than for montmorillonite. Still, the difference may not be dramatic.
4. Palygorskite should have a higher ion diffusion capacity than smectitic clays because the amount free water is higher and the net lattice charge lower. Hence, D_e for the considered cation is expected to be slightly higher than for the mixed-layer smectite-mica clay. However, due to the rather significant anion sorption and exchange capacities, D_e for anions should be lower than for all the smectitic clays.
5. Kaolinite has the highest cation diffusion capacity than the other clays because the amount free water is higher and the net lattice charge very low. However, the anion adsorption capacity is rather significant, especially if the clay is very fine-grained, and the anion diffusion capacity may therefore not be the highest.

Since the buffer is aimed at minimizing diffusive transport of radionuclides and corrodants, montmorillonite-rich clay like MX-80 is advantageous. Saponite is comparable with MX-80 while mixed-layer smectite-mica is less good and palygorskite and kaolinite even less suitable except for anion transport, at least if the grain size is very small.

4.4 Thermal conductivity

The thermal conductivity is essential in two respects. Firstly, a poor conductivity may raise the temperature in the buffer to a level that threatens its physico/chemical stability. Secondly, the temperature of the canister may become unsuitably high. The conductivity depends strongly on the water content, which will drop by dessication in the canister-embedding part of the buffer and rise in the peripheral part contacting the surrounding, colder rock. If the temperature close to the canister rises to more than 120-150°C, the vapor pressure may be high enough to make water in vapor form dissipate upwards through the drying buffer when the porewater pressure in the nearfield has not yet increased sufficiently much. Thus, the "effective" thermal conductivity in the earliest phase, being approximately equal to that of the buffer with its original water content, controls the heat dissipation and the physical state of the buffer.

The location and state of the porewater is essential and there is a direct analogy between the electrical conductivity, as indicated in Figure 15, and the thermal conductivity. Thus, smectite minerals holding interlamellar water and also being surrounded by water hulls that overlap and join, provide better heat conduction than most other minerals that establish contact only over very small surfaces. The thermal conductivity is affected also by the content of effectively heat-conducting minerals like quartz.

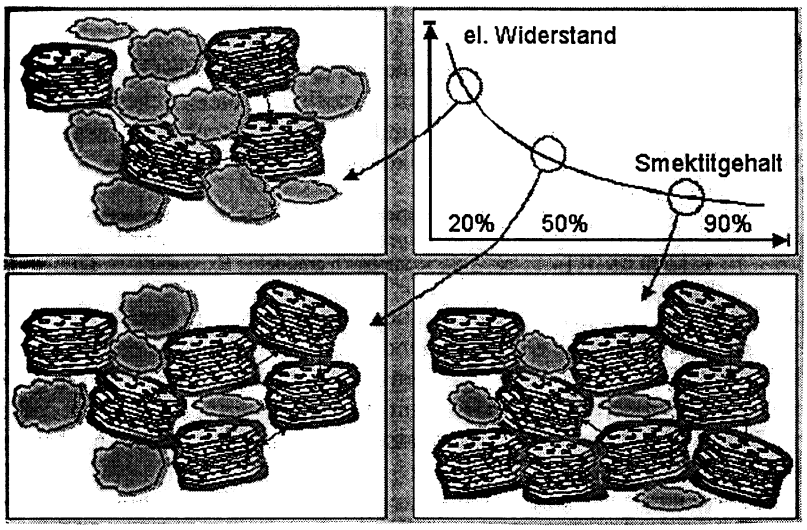


__Figure 15__. Schematic picture of the importance of hydrated minerals (smectites) for the electrical conductivity [21]. The grey grains, which prevent contact between the smectite stacks at low smectite contents, are assumed to have a poor electrical and heat conductivity.

The thermal conductivity of soil constituents ranges from about 0.25 W/m,K for very porous minerals to 8.4 W/m,K for quartz. Many rock-forming and clay minerals like mica and kaolinite have a conductivity on the order of 2.0 W/m,K.

Using current methods for calculating the bulk thermal conductivity of soils, which imply that it is strongly affected by the volumetric proportions of the various constituents and by the porosity, the thermal conductivity can be predicted. Taking the water content as 10 % of all the investigated clay types one would hence expect the bulk thermal conductivity to be as indicated in Table 2.

Table 2. *Expected thermal conductivity of clays with a water content of 10 %**

Clay type	**Dry density 1600 kg/m^3**	**Dry density 800 kg/m^3**	**Remark**
Saponite	0.5-0.7	0.2-0.4	Little water in interconnected hulls
Mixed-layer smectite-mica	0.6-0.8	0.2-0.4	Some water in interconnected hulls
Kaolinite	0.8-0.9	0.3-0.5	All water in interconnected hulls
Palygorskite	0.3-0.5	0.1-0.2	No water in interconnected hulls
Montmorillonite	0.5-0.7	0.2-0.4	Little water in interconnected hulls

* Calculated by Sven Knutsson, Luleå Technical University

The thermal conductivity is expected to be highest for the mixed-layer smectite-mica and kaolinite but the difference between the various clays is assumed to be moderate except for palygorskite, which is estimated to be the least effectively heat-transferring clay type for a water content of 10 %.

4.5 Rheology

4.5.1 Basic

In the present context the major rheological properties are the swelling potential and pressure since they determine the self-sealing capacity of the clay and the ability of the buffer clay to establish a tight contact with the rock surrounding the deposition holes. The creep behavior is referred to as well [9].

4.5.2 Swelling pressure

The expandability and swelling pressure depend on the hydration potential of the clay minerals and the following ranking is therefore expected (cf. Section 4.2):

1. Montmorillonite is the most hydrophilic smectite mineral and has the largest specific surface area, which means that montmorillonite-rich clay has a very substantial swelling pressure. At high densities the swelling pressure is at maximum when the clay is Ca-saturated, while the pressure drops considerably at reduced density and vanishes at about 1600 kg/m^3, cf. Figure

16. The expansion potential – several hundred percent in fresh water- is due both to the fact that the interlamellar space can host three hydrate layers in contrast to other smectites, and that the gel-forming capacity is very strong except when the porewater salinity is high.

2. Palygorskite is hydrated in conjunction with strong structural rearrangement. The swelling of palygorskite has been reported to be almost the same as for Na montmorillonite. The thixotropy is very substantial, suggesting that the gel-forming capacity is very high. However, it is suspected that it may not be so on a microscopic level.

3. Saponite behaves, in principle, like Ca-montmorillonite and hence has a very high swelling pressure at high densities and a somewhat smaller expandability than Na-montmorillonite. For low densities saponite is hence expected to exert an appreciably lower swelling pressure than equally dense Na-montmorillonite.

4. Mixed-layer smectite-mica should naturally have a significantly lower swelling pressure and expandability than the smectites. Still, the hydration potential is relatively high and the expandability important for high densities.

5. Kaolinite has a very low hydration potential and not unless the clay is compacted to high densities, a swelling pressure is produced. There is almost no expandability except, possibly, if the clay is very fine-grained.

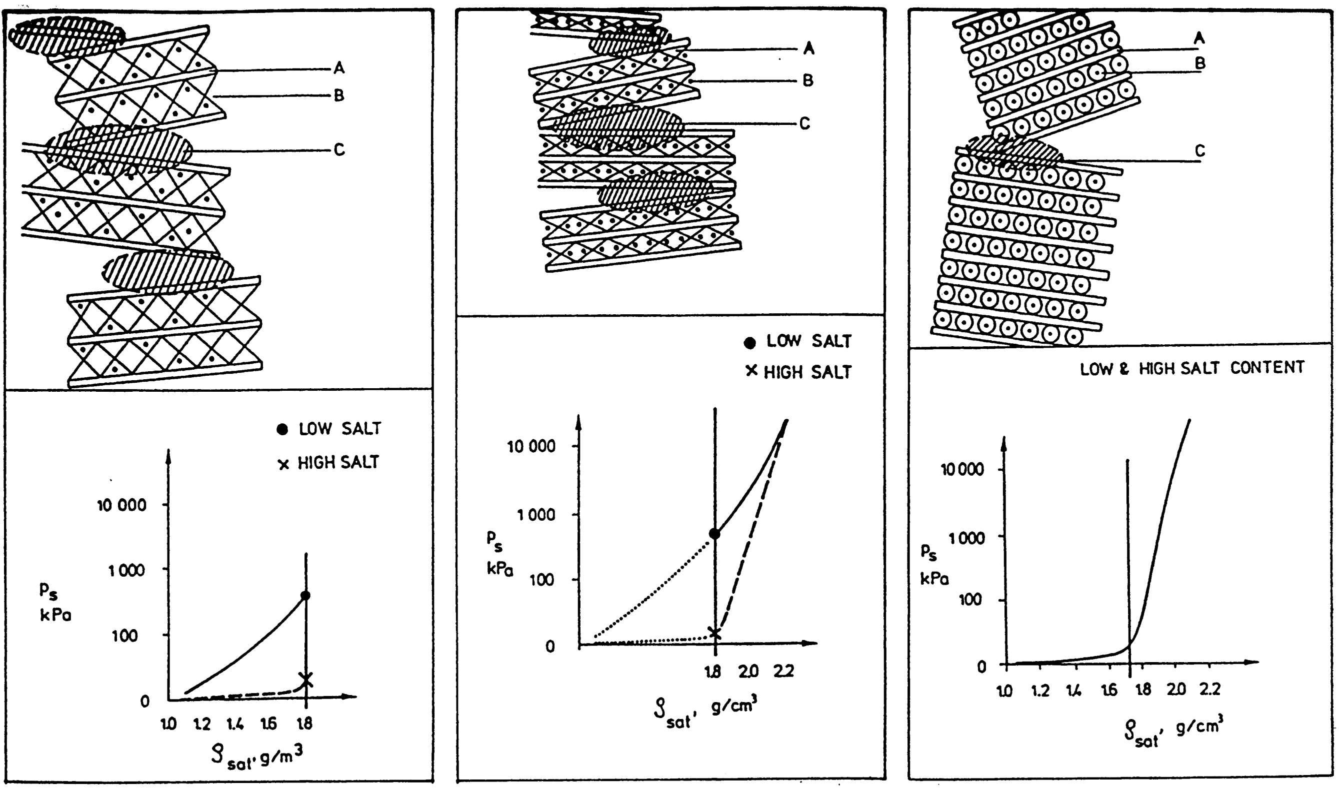


Figure 16. Stack assemblages and influence of density at saturation for montmorillonite. A) Lamella; B) Interlamellar space; C) Stack contact with interacting electrical double-layers. Left and middle: Na clay. Right: Ca clay [22].

4.5.3 Creep

A high creep potential is valuable for the homogenization of the buffer but negative for time-dependent canister movement. The creep rate for shear stresses induced by canister loads (roughly 100-200 kPa) should be retarded and very moderate. The parameters used for characterizing the creep behavior of clays are A, B and t_o defined as in Eq.1 and 2, which represent the log-time creep law that most soils obey [8,9,23]. The experimental performance is illustrated in Figure 17.

$$\gamma = B \ln(t + t_o) + A \qquad (1)$$

$$d\gamma/dt = B\,(t + t_o)^{-1} \qquad (2)$$

where γ= Angular strain
A= Constant
B= Inverted shear modulus (high values denote low shear modulus and high values stiff behavior)
t_o= Shape of initial part of the creep curve. Negative values indicate very quick reduction in creep rate

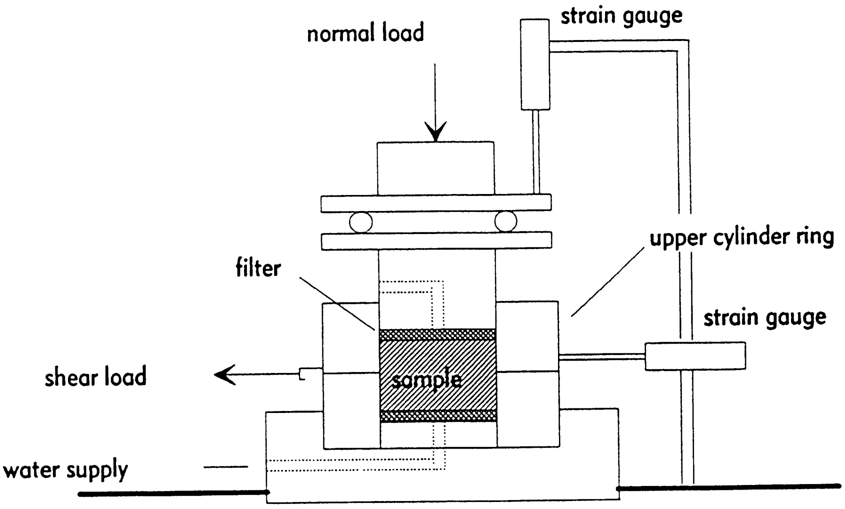


Figure 17. Schematic picture of the shear box used for creep testing.

Saponite

Water saturated saponite has about the same rheological properties as montmorillonite for bulk densities representing buffer clay. The fact that only 2 interlamellar hydrates can be formed [14] means that saponite with Na or Ca as montmorillonite saturated with Ca. One earlier described implication of this would be that the gel-forming capacity and hence homogenization potential is not as good as that of montmorillonite and in the present context it may imply that the friction angle is lower and the creep strain rate higher at any stress level than the corresponding properties of montmorillonite [8]. However, the difference between the two smectite species is probably not very significant.

Mixed-layer smectite/mica

The creep rate of mixed-layer smectite/mica is estimated to be approximately proportional to the smectite content. If this content is 50 % of that of pure montmorillonite clay the creep rate under identical stress conditions is expected to be significantly lower than that of montmorillonite.

Kaolinite

Kaolinite has approximately the same consistency limits as fine quartz-rich silt, which suggests that the shear strength at bulk densities similar to those of buffer clay is high. Thus, the friction angle is expected to be at least 25° and the creep rate low and strongly retarded under the expected stress conditions.

Palygorskite

For densities typical of buffer material palygorskite is expected to have a very high shear strength and exhibit little creep because of the effective physical particle/particle contacts. For the density that is achieveable by applying 100 MPa compaction pressure the effective interfingering and mechanical interaction of the numerous fiber particles is expected to be very good and the shear strength significantly higher than that of the other clay types.

Montmorillonite

The gel-forming potential of montmorillonite is very good when saturated with Na, while it is less good for Ca-saturation. The better homogeneity of Na montmorillonite yields a slightly higher friction angle than of Ca montmorillonite but both forms are high-plastic clays with significant creep properties for bulk densities representative of buffer clay.

The creep strain under the stress conditions in deposition holes is expected to be highest for montmorillonite and saponite, lower for mixed-layer smectite-mica and even lower for kaolinite. Palygorskite is expected to exhibit less creep than the other clay types.

4.6 Longevity

4.6.1 General

While the long term chemical stability of montmorillonite has been extensively investigated, the understanding of the survival potential of other clay mineral types is limited. The basis of any estimation of the longevity of buffer clay under repository conditions should be fundamental thermodynamics and geological evidence, which are taken as a basis of the present discussion. The most important stability-controlling factors are the critical temperature for alteration with special respect to the groundwater chemistry (salt, pH), and the physical properties of the reaction products.

4.6.2 Saponite

The most probable degradation of saponite buffer clay is alteration to corrensite and chlorite [24]. Corrensite, which is a mixed-layer mineral composed of aluminous saponite and chlorite, appears to retain its expandability at temperatures up to 150-200°C. It can be further altered to discrete chlorite and illite, which both have a cation exchange capacity of about 30 meq/100 g and some minor expansion potential. If the bulk density of saponite as buffer remains high (2000 kg/m^3), the reaction product is expected to have a relatively low hydraulic conductivity, probably similar to that of mixed-layer smectite-mica clay with about 50 % expandables.

Saponite is considered to be the most stable smectite species [25], which has made this clay mineral particularly suitable as drilling mud at large drilling depths. It is hence believed to be superior to montmorillonite as concerns longevity. Under the conditions prevailing in a KBS3 repository, saponite as buffer material should hence remain largely intact after 100 000 years if the temperature is maintained below 100°C for a few thousand years and then reduced to the normal bedrock temperature. As for montmorillonite some slight cementation may take place in the buffer by dissolution of silica in the hottest part and precipitation in the colder clay.

4.6.3 Mixed-layer smectite-mica

Basically, mixed-layering means mixing of different mineral layers in a single coherent, stacked structure. Hydrous montmorillonite has crystal lattice parameters that approach those of mica and therefore facilitates montmorillonite/mica stacking as in Friedland clay [24].

Mixed-layer clay of the presently investigated type contains about 45 % expandables of which montmorillonite makes up around 25 % and this mineral is the most vulnerable one under repository conditions. The expected degradation is conversion to illite or possibly mixed-layer motmorillonite/illite, which is hence the same mechanism that is believed to alter montmorillonite of MX-80 type to nonexpanding clay. It requires access to free potassium, which is not readily available in the clay because the only K-bearing mineral is the very stable mica component. Hence, external K is required to illitizise the smectite. This process is very slow as demonstrated by the extensive work on the stability of MX-80 buffer [10] but since the smectite content is only 30-40 % of that of MX-80, the time for very significant degradation of the buffer is shorter. Still, for temparatures in the range of 80-100°C it would take tens of thousands of years before a mixed-layer smectite-mica buffer clay is altered to a large extent. It is expected that even complete change of the smectite component to non-expandable minerals would not yield a very significant change in hydraulic conductivity, while the swelling pressure and expandability will be largely lost.

Of the other major components, quartz and 14Å-chlorite, the firstmentioned is very stable while chlorite may be decomposed for pH<7. However, this chlorite species is known to be very stable at much higher temperatures than 100°C under neutral and higher pH conditions, which are expected in the buffer [25].

4.6.4 Kaolinite

Use of geochemical codes have given stability diagrams of the sort shown in Figure 18, which imply that kaolinite is favored over illite, montmorillonite and feldspar phases by low alkali$^+$/H$^+$ ratios, i.e. under slightly acid conditions with some slight amount of dissolved silica available. An increase in pH decreases the stability of kaolinite that tends to undergo conversion to gibbsite, an aluminum hydroxide with kaolinite-like behavior, while a drop in pH alters the kaolinite to smectite. Kaolinite together with smectite is stable up to about 200°C and with mixed-layers it may be stable up to 250 °C.

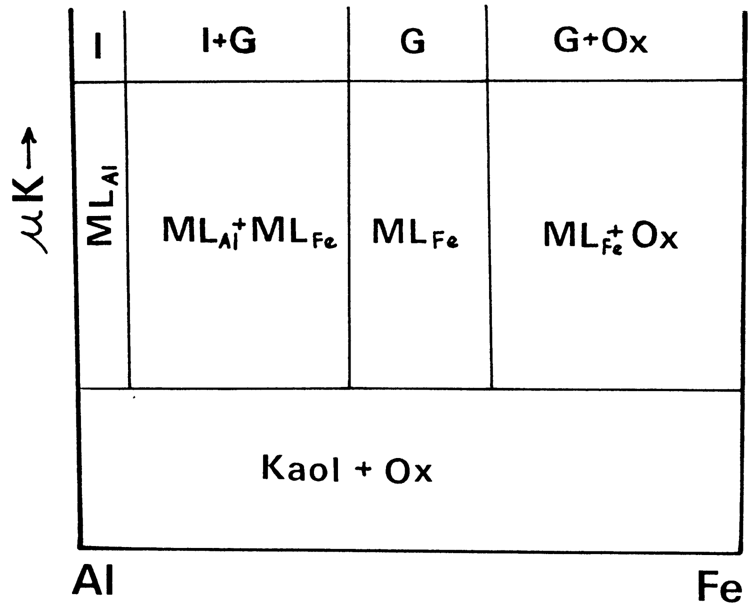


Figure 18. *Schematic phase relations showing the tendency of kaolinite alteration to smectites and further to illite (I) and glauconite (G) at increasing potassium content in the porewater. Ox denotes iron oxide,* ML_{Al} *mixed-layer aluminous smectite-illite, and* ML_{Fe} *mixed-layer Fe-rich galuconite and smectite-mica [24].*

The indication that the most probable alteration product at normal and slightly higher pH may be smectitic mixed-layer minerals suggests that the physical properties of a clay buffer of pure kaolinite in fact improve. If the clay contains much soluble silica and pH is low or pK$^+$ very high, K-feldspars may form even at room temperature (Figure 19) but these conditions are not plausible in the buffer.

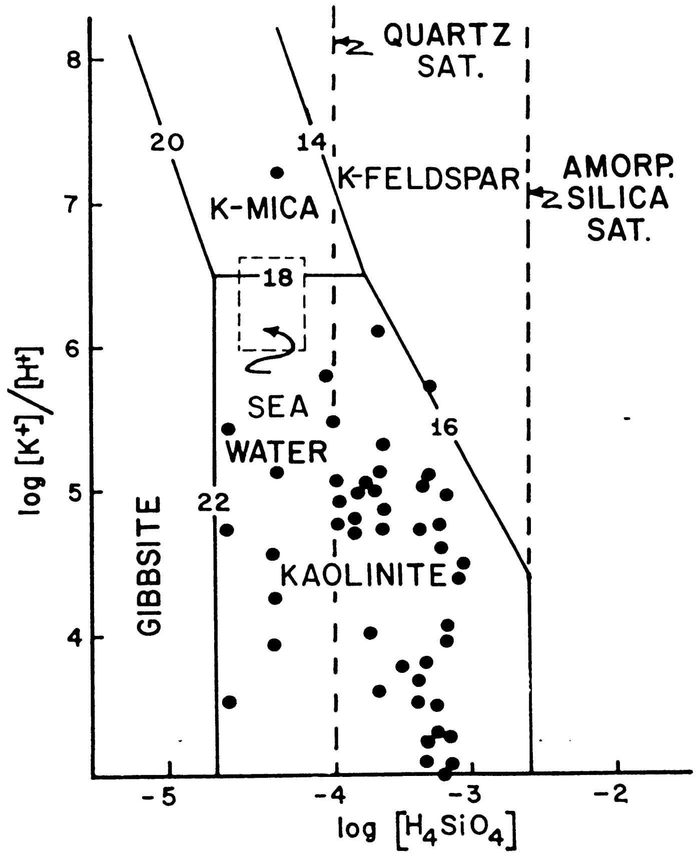


Figure 19. *Probable stability relations in the* K_2O-AL_2O_3-SiO_2-H_2O *system [26].*

4.6.5 Palygorskite

The general stability conditions of palygorskite are illustrated in Figure 20. This mineral is stably associated with smectites, dioctahedral as well as trioctahedral, which demonstrates that these minerals have similar stability properties. This is supported by the fact that palygorskite appears in Paleozoic deep sea and shallow marine deposits just like smectites, and also that palygorskite and smectites usually form interfingering or adjacent bodies.

The frequent use of palygorskite as drilling mud in boring of deep holes in the former Soviet Union demonstrates that the thermal stability under highly saline conditions is higher of palygorskite than of montmorillonite [5]. Cyclic heating up to 180°C yielding complete drying does not lead to permanent collapse as in montmorillonite, presumably because the surface properties of palygorskite are determined by the crystal lattice while those of montmorillonite are largely controlled by adsorbed cations.

In conclusion, the stability of palygorskite is believed to be higher than that of montmorillonite, while it is estimated to be similar to that of saponite.

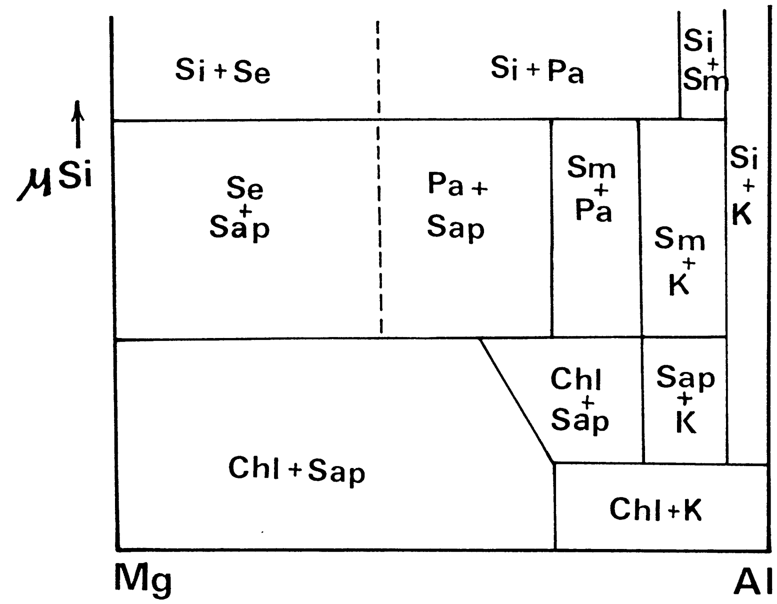


Figure 20. Proposed phase relations in Mg-Al-Si system showing the close relationship between palygorskite and smectites. The chemical potential of free silica Si is continuously variable in the diagram. Pa=palygorskite, Se=sepiolite, Chl=chlorite, Sap=saponite, Sm=smectite (montmorillonite), K=kaolinite [25].

4.6.6 Montmorillonite

The stability of montmorillonite is concluded to be controlled by the rate of conversion to illite through intermediate smectite/illite mixed-layer formation, or by neoformation of illite. At temperatures below about 100°C the rate of potassium uptake controls the conversion rate, which can be expressed as an Arrhenius-type function [10]. The activation energy is assumed to be in the interval 26-28 kcal/mole, which theoretically yields a reduction in montmorillonite from originally 70 % to no less than 50 % after 3000 years at 100 °C at the normal potassium content in deep Swedish groundwater.

Natural bentonite beds that have been exposed to temperatures in the range of 140-160°C for about 300 years, 120-140° for another 300 years and to 100-120°C for an additional period of 500 years, have undergone slight cementation by precipitated silica [27], and this has been considered as a potential risk since such cementation will reduce the expandability of the buffer clay. However, ongoing research indicates that this risk is small or even negligible for temperatures below 100°C also considering the temperature gradient across the buffer that in fact controls the transport and precipitation of silica.

The chemical stability of palygorskite and kaolinite under repository conditions appears to be better than that of smectitic clays. Since the present understanding is that the stability of montmorillonite in the form of MX-80 is acceptable, the other clay types investigated here are all sufficiently stable to be accepted as buffer materials.

4.7 Preliminary assessment of buffer of different clay types with respect to their physical properties

Since the alternative clay buffer materials are concluded to be at least as stable as montmorillonite from a chemical point of view or yield acceptable reaction products, they should be assessed on the basis of their physical properties.

Scoring can be made on the basis of the general statements given in the preceding text but the relative importance of the physical properties can be discussed. A preliminary ranking based on the five most important physical properties, i.e. the hydraulic conductivity, diffusion retardation, expansion potential, thermal conductivity, and creep disposition, would be that in Table 3. This simple comparison implies that the various properties have equal weight, which is certainly debatable.

Table 3. *Preliminary assessment of the investigated clay types. *** is top quality, ** medium quality, and * low quality. Hydraulic conductivity=K, Diffusion retardation=D, Expansion potential=E, Thermal conductivity=T, Creep disposition=C. The thermal conductivity refers to 10 % water content.*

Clay type	**K**	**D**	**E**	**T**	**C**	**Sum**
Saponite	***	***	***	**	*	12 *
Mixed-layer smectite-mica	**	**	**	***	**	11 *
Kaolinite	*	* (***)1)	*	***	***	9 * (12 *)1)
Palygorskite	**	**	***	*	***	11 *
Montmorillonite	***	***	***	**	*	12 *

1) Estimated for very fine-grained kaolinite, especially referring to anion diffusion

With the assumed basis of scoring the difference between the considered clay types is surprisingly small, provided that the expected and in some cases assumed performances are correct. In fact, the clays are almost equally good if the kaolinite clay is prepared in very fine-grained form.

Scoring on the basis of weighted performances requires that the degree of importance of the respective function must be relevant and it is proposed here to consider the hydraulic conductivity, the thermal conductivity and the creep behavior as being most important. Ascribing to them a multiplication factor 3 and 1 to the other ones one finds that the clay candidates still have about the same scorings, but with the mixed-layer clay being superior to the others.

Considering also other functions of importance, like the critical gas pressure and the ion diffusion capacity, one still finds no major difference in scoring and other properties, like the cost and availability and practical issues like the compactability, may therefore be decisive. Most important is of course that the various physical properties need to be validated. This is the issue of the subsequent chapter.

5 EXPERIMENTAL

5.1 Program

Following the scheme for characterizing buffer clay candidates in Chapter 4, test data of commercially available materials representing saponite, mixed-layer smectite-mica, kaolinite, and palygorskite have been collected for comparison with typical data of SKB's reference buffer clay MX-80. The data concern:

- Mineralogical composition
- Chemical composition
- Granulometry
- Hydraulic conductivity
- Diffusion capacity
- Thermal conductivity
- Swelling pressure
- Rheology

5.2 Mineralogical composition

Table 4 shows the mineralogical composition of the investigated clays (weight percent).

Table 4. Approximate mineral composition of the investigated clays.

Clay	**Smectite**	**Palygorskite**	**Mixed-layer**	**Chlorite**	**Kaolinite**	**Quartz**	**Feldspar**	**Mica**
Saponite	70	-	-	-	-	10-15	10-15	10-15
Mixed-layer	- 1)	-	45	10-15	3-5	20-25	5	10-15
Kaolinite	5-10	-	-	-	75	15-20	-	-
Palygorskite	10-15	80	-	?	-	5	-	-
Montmorillonite (MX-80)	70-80	-	-	-	2-5	10-15	10-15	5

1) Total weight fraction of smectite in mixed-layer minerals=50 %

The fact that none of the investigated clays is very pure is typical of large mineral deposits. However, the respective major mineral is suffiiciently dominant to be a determinant of the physical performance in bulk. The palygorskite clay has an exceptional quality; it is significantly richer in the mineral palygorskite than most sources that are exploited commercially.

It should be noted that all the clays have a considerable quartz content except the palygorskite clay. Both the kaolinite and palygorskite clays contain around 10 % smectite.

5.3 Chemical composition

Table 5 shows the chemical composition of the investigated clays in bulk form. The difference between these values and those in Table 1 is caused by the fact that the clays are commercial brands that contain several accessory minerals. These represent at least 25 % of the respective main clay material (Table 4).

***Table 5.** Typical chemical composition of the investigated clay types in weight percent (bulk). Deviation from 100 % is due to missing "oxides".*

Clay	**SiO_2**	**Al_2O_3**	**Fe_3O_3**	**MgO**	**K_2O**	**Na_2O**
Saponite	61.6	9.8	3.0	20.0	2.0	0.9
Mixed-layer	56.8	17.6	4.5	2.0	2.7	0.9
Kaolinite	54.5	32.5	0.35	0.15	0.22	0.01
Palygorskite	45-55	10-14	1-2	5-9	-	-
Montmorillonite (MX-80)	63.8	19.8	5.0	3.2	1.0	2.8

5.4 Granulometry

The grain (granule) size distribution of the clay materials in air-dry, ground form is given in Table 6. The clay content (<2μm) of dispersed material is shown in Table 7.

***Table6.** Grain (granule) size distribution (amount in weight percent).*

Clay	**<63 μm**	**<125 μm**	**<250 μm**	**<500 μm**	**<1 mm**
Saponite	20	30	60	90	100
Mixed-layer	20	50	75	95	100
Kaolinite	0	1	20	75	100
Palygorskite	10	30	60	90	100
Montmorillonite (MX-80)	15	28	55	99	100

***Table 7.** Clay content of dispersed material (Weight percentage of particles <2μm).*

Clay	**Clay content, %**
Saponite	75
Mixed-layer	55
Kaolinite	58
Palygorskite	79
Montmorillonite (MX-80)	80

The content of particles finer than 2 μm in dispersed form is lower for kaolinite than for the other clays despite its higher purity. This demonstrates that the kaolinite particles are made up of rather thick stacks of strongly attached lamellae that are not readily disintegrated.

5.5 Hydraulic conductivity

5.5.1 Recording

The hydraulic conductivity is determined by use of oedometers in which the clay is applied in the form of air-dry powder that is wetted by absorption of water under confined conditions. The hydration is associated with the build-up of a swelling pressure that is recorded in the course of the wetting. Since the porosity can be calculated on the basis of the initial water content and the bulk density [28], one can determine the amount of pore liquid that is required to reach saturation. Recording the water uptake can hence tell when complete saturation has been obtained.

For smectite clays the hydration potential of air-dry powder is so high that complete saturation takes place by suction, while for others, a slight overpressure may have to be applied to get them fully saturated. Smectite clays exert a considerable swelling pressure on the cell walls, which eliminates water leakage along the clay/walls in the conductivity measurements, but such leakage can take place when testing clays with low pressure potential. In the last-mentioned case, the cell walls must be threaded and the threads filled with dense smectite [29].

For making comparison of the various clays possible the conductivity data are given for a density that can be obtained by compacting powder under 100 MPa pressure, i.e. 2000 kg/m^3 for the clays dominated by saponite, mixed-layer smectite-mica, kaolinite, and montmorillonite (MX-80), and 1650 kg/m^3 for the palygorskite-rich clay. For illustrating the influence of density changes on the microstructural homogeneity and hence the gel-forming capacity, the conductivity for a lower density, 1800 kg/m^3 and 1550 kg/m^3, respectively, is given as well.

The reason for the much lower bulk density of the palygorskite clay is the low specific density 2330 kg/m^3, which is appreciably lower than the specific density of the other clays (2600-2700 kg/ m^3).

5.5.2 Conductivity data

The hydraulic conductivity of the investigated clays has been determined by Clay Technology, Lund, and DURTEC, Neubrandenburg (Germany), [6]. Both distilled water and 3.5 % $CaCl_2$ solution were used for most of the testing, which gave the data in Table 8 for distilled water and in Table 9 for the salt percolate.

Table 8. *Hydraulic conductivityK in m/s for percolation with distilled water [6,8].*

Clay	**Bulk density at saturation, kg/m^3**	***K*, distilled water**
Saponite	1800	E-12
”	2000	5E-13
Mixed-layer	1800	5E-11
”	2000	4E-12
Kaolinite	2000	2E-10
Palygorskite	1550	3E-11
”	1650	E-12
Montmorillonite (MX-80)	1800	9E-13
”	2000	4E-13

Table 9. *Hydraulic conductivityK in m/s for percolation with 3.5 % $CaCl_2$ [6,8].*

Clay	**Bulk density at saturation, kg/m^3**	***K*, 3.5 % $CaCl_2$**
Saponite	-	-
Mixed-layer	1800	E-10
”	2000	2E-11
Kaolinite	2000	2E-10
Palygorskite	1550	5E-11
”	1650	4E-12
Montmorillonite (MX-80)	1800	2E-11
”	2000	2E-13

The following observations are made:

1. All the clays except kaolinite have a conductivity lower than 2E-11 m/s for a density obtained by compacting the clay powder under 100 MPa pressure.

2. MX-80 and saponite are much less permeable than the other clays.

3. Kaolinite is significantly more permeable than the other clays.

4. Palygorskite is about ten times more permeable than the smectites but equally permeable as the mixed-layer clay.

5. The conductivity of all the clays except kaolinite and palygorskite is 5-10 times higher for percolation with strong Ca-solution than when distilled water is permeated. This shows that chemically induced microstructural changes of kaolinite and palygorskite are very small.

The expected difference in hydraulic conductivity between the five clay types that was deduced on the basis of microstructural modeling and typical

hydration properties in Section 4.3.2 is almost completely validated by the actual test data. With respect to the buffer criteria specified in Chapter 2 it is concluded that all the clays qualify except the kaolinite clay. However, fine grinding may bring down the coductivity to an acceptable level.

MX-80 is preferable

5.6 Ion sorption and diffusion

5.6.1 Cation exchange

The cation exchange capacity, determined by applying the DIN/ISO 11260 standard, implying pretreatment with Ba and subsequent addition of $MgSO_4$ for complete Mg saturation. The data are given in Table 10.

Table 10. *Cation exchange capacity (CEC) in meq/100 g*

Clay	**CEC, meq/100 g**
Saponite	110
Mixed-layer	60
Kaolinite	10-15
Palygorskite	19-21
Montmorillonite (MX-80)	102-140

One finds that the two clays containing the smectites saponite and montmorillonite have the highest cation exchange capacity and that kaolinite and palygorskite have the lowest, which is in complete agreement with the predictions in Section 4.3.5. The mixed-layer clay has a somewhat higher CEC than expected, probably due to the contribution by very fine mica [29].

5.6.2 Diffusivity

The diffusive transport capacity, expressed in terms of the effective diffusion coefficient, has only been determined for montmorillonite, but one can estimate whether it should be lower or higher for the other clays on the basis of their microstructural constitution. Thus, recent investigations of ion diffusion show that in clays with very narrow void systems and high cation sorption capacity like montmorillonite and saponite the diffusive transport is significantly delayed by drag effects and surface complexation [18], while this is not the case for kaolinite. Mixed-layer minerals would be intermediate in this respect. Delay in ion migration caused by sorption (K_d) effects should be small in palygorskite while migration of hydrated cations in the narrow channel network of the palygorskite should be delayed by geometrical restrictions at least of strongly hydrated cations.

The exclusion of anions from the large majority of the voids in the two smectites means that the anion diffusion capacity is appreciably lower than that of the other clays.

It is expected that kaolinite has the highest cation and anion diffusion transport capacity and that mixed-layer clay and palygorskite come second and third. Saponite is inferior to montmorillonite since its gel-forming and diffusion-retarding potential is lower. It is hence believed that montmorillonite is the most effectively diffusion-retarding clay, while kaolinite is the least effective.

MX-80 is preferable

5.7 Thermal conductivity

The thermal conductivity has been determined of two of the clays, saponite and montmorillonite (MX-80), and no general comparison of the five clay types can therefore be made. However, earlier tests on a mixed-layer clay (Fo-Ca7, the French candidate clay), with smectite-kaolinite as dominant mineral and with 5-10 % kaolinite, about 5 % smectite, and 5 % quartz as well as some minor accessory constituents like hematite, gypsum and calcite [3] have given relevant conductivity data which are approximately representative of the mixed-layer smectite-mica clay. Recorded data for the three investigated clays are summarized in Table 11.

Table 11. *Thermal conductivity λ data of saponite and montmorillonite (MX-80), [8], and mixed-layer clay [3]. The dry bulk density was about 1800 kg/m^3.*

Clay	**Water content, %**	**λ, W/m,K**
Saponite	13.4	0.35
Mixed-layer smecticte/kaolinite	10.0	1.6-1.8
Montmorillonite (MX-80), Na-form	10.0	0.65
Montmorillonite (MX-80), Ca-form	17.0	0.73

The thermal conductivity of Na montmorillonite is on the same order of magnitude as the theoretically deduced value for 10 % water content. For Ca montmorillonite the water content was higher and the conductivity therefore higher. Saponite has a significantly lower conductivity than montmorillonite, although they were expected to behave similarly according to the deduction in Section 4.4.1. This can not be readily explained at the moment although it may be that the content of mica in the saponite reduced the interconnectivity of the smectite component and thereby gave a lower λ-value. Information from ENRESA yields higher values than the one reported here [1].

A remarkable fact is the very high thermal conductivity of the mixed-layer clay; it was in fact considered to be a primary factor in the process of selecting a suitable buffer for the French concept.

It is concluded that the thermal conductivity of the montmorillonite-rich clay is on the same order of magnitude as predicted on a theoretical basis (Section 4.4.1, Table 2), while the mixed-layer clay turned out to be much more conductive than predicted. The saponitic clay appears to have a lower conductivity than montmorillonite.

Mixed-layer smectite-mica clay is preferable

5.8 Swelling pressure

5.8.1 Recording

The standard procedure is that the swelling pressure is determined by use of oedometers in which the clay is applied in the form of air-dry powder that is wetted by absorption of water under confined conditions. The hydration, which is of diffusion type, is associated with the build-up of a swelling pressure that is recorded in the course of the wetting (Figures 21 and 22). The rate of pressure growth increases with the hydrophilicity and is reduced with dropping hydraulic conductivity in a complex fashion that is basically controlled by the microstructure.

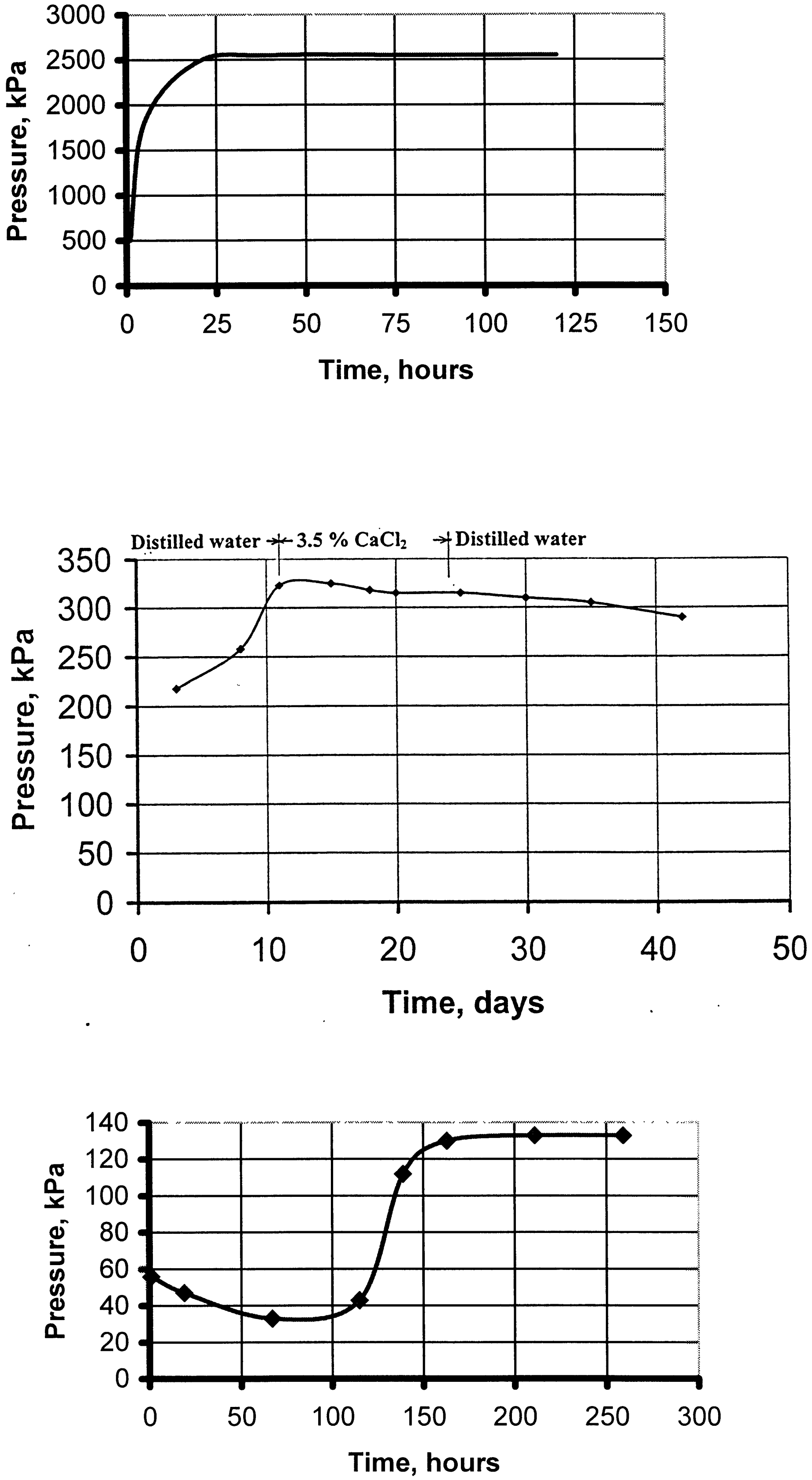
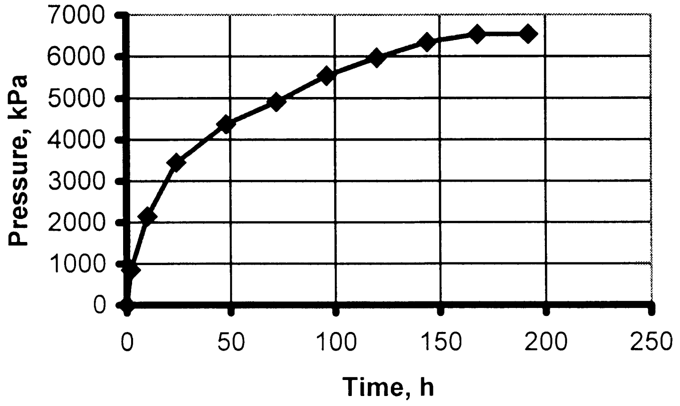


Figure 21. *Development of swelling pressure of the investigated clays. Upper: Saponite (1720 kg/m^3). Middle: Mixed-layer (1900 kg/m^3).Lower:Kaolinite (2000 kg/m^3).*



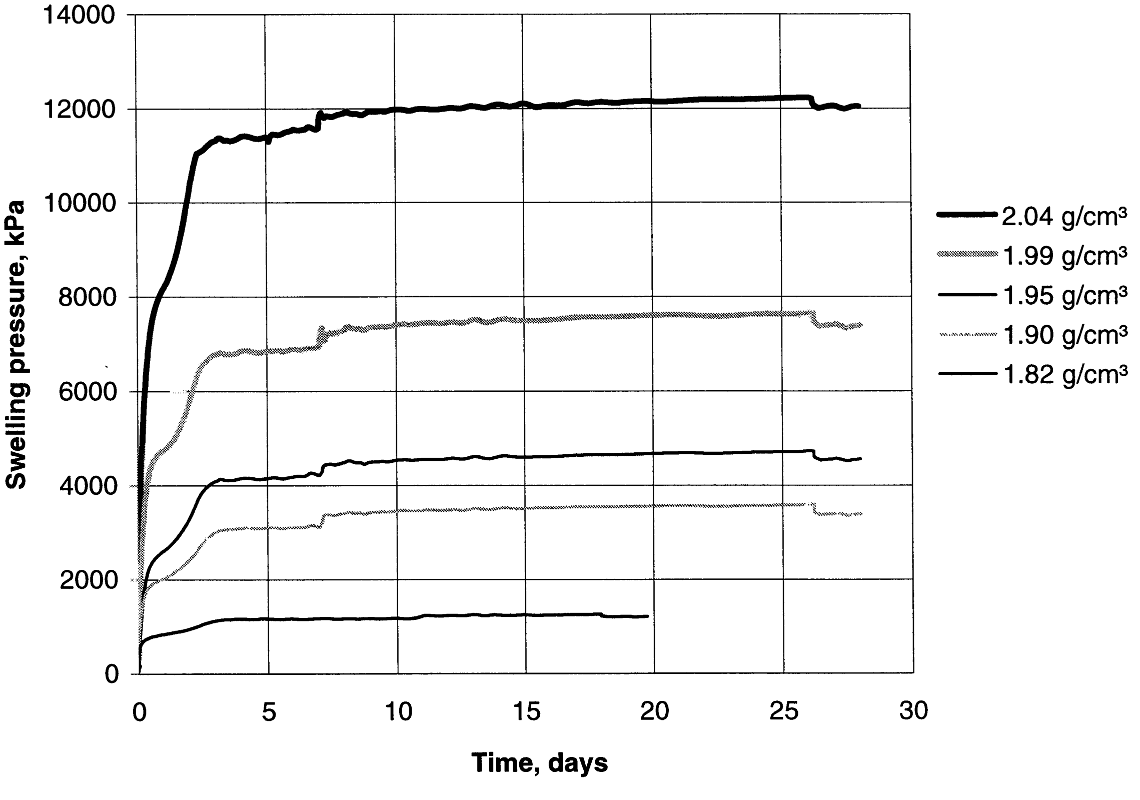


Figure 22. *Development of swelling pressure of the investigated clays. Upper: Palygorskite (1650 kg/m³). Lower: Montmorillonite (densities 1820 to 2040 kg/m³).*

The size and shape of the samples were all the same and the diagrams can therefore be directly compared. One concludes that the evolution pattern of the swelling pressure is not the same. Thus, the hydration of saponite and montmorillonite is quickest, while that of palygorskite is relatively slow. The behavior of kaolinite is intermediate. It may be that while the hydrophilicity of both the smectites and palygorskite is very high the narrow channel network of the palygorskite offers a higher resistance to water migration and hence delayed wetting. For kaolinite the microstructural changes associated with hydration are small and the interconnected voids rather large, yielding quick capillary flow and saturation.

5.8.2 Pressure data

As for the hydraulic conductivity, the pressure data are given below for a density that can be obtained by compacting powder under 100 MPa pressure, i.e. 2000 kg/m^3 for the saponite, mixed-layer, kaolinite, and montmorillonite (MX-80), and 1650 kg/m^3 for palygorskite. For illustrating the influence of density changes on the microstructural homogeneity, the swelling pressure for a lower density, 1800 kg/m^3 and 1550 kg/m^3, respectively, is given as well.

The swelling pressure of the investigated clays has been determined by Clay Technology, Lund, and DURTEC, Neubrandenburg (Germany), [6]. Both distilled water and 3.5% $CaCl_2$ were used for most of the testing, which gave the data in Table 12 for distilled water and in Table 13 for the salt water.

Table 12. *Swelling pressure p_s in kPa for saturation with distilled water [6,8].*

Clay	**Bulk density at saturation, kg/m^3**	**p_s, Distilled water**
Saponite	1800	2500
”	2000	8800
Mixed-layer	1800	150
”	2000	1050
Kaolinite	2000	130
Palygorskite	1550	400
”	1650	6500
Montmorillonite (MX-80)	1800	600
”	2000	7300

Table 13. Swelling pressure p_s in kPa for saturation with 3.5 % $CaCl_2$ [6,8].

Clay	**Bulk density at saturation, kg/m^3**	**p_s, 3.5 % $CaCl_2$**
Saponite	-	-
Mixed-layer	1800	150
”	2000	1000
Kaolinite	2000	120
Palygorskite	1550	320
”	1650	5650
Montmorillonite (MX-80)	1800	200
”	2000	4700

It is concluded that saponite compacted under 100 MPa pressure gives a somewhat higher swelling pressure than the montmorillonite clay while palygorskite saturated with distilled water gives approximately the same pressure. However, at saturation with salt Ca-rich water palygorskite gives a higher pressure than montmorillonite, which verifies that chemically generated microstructural changes are rather significant in montmorillonite but small in palygorskite. Kaolinite gives very low swelling pressures; it behaves almost as a hydrophobic material.

The expected difference in swelling pressure between the five clay types that was deduced on the basis of microstructural modeling and typical hydration properties in Section 4.5.2 is almost completely validated by the actual test data. With respect to the buffer criteria specified in Chapter 2 it is concluded that all the clays qualify with the possible exception of the kaolinite clay, which may give a somewhat too low contact pressure between the rock and the canister. However, fine grinding may bring down the coductivity to an acceptable level. Palygorskite provides a substantial swelling pressure pressure that is almost unaffected by the porewater chemistry.

Palygorskite is preferable

5.9 Rheology (Creep)

5.9.1 General

Creep tests have been made on the clays dominated by saponite and montmorillonite (MX-80) as well as on the mixed-layer smectite-kaolinite clay mentioned earlier [3]. The latter is believed to be approximately representative of the smectite-mica clay. The other clays have not been investigated and no final assessment can therefore be made. Typical data are collected in Table 14.

Table 14. *Typical creep parameter data for the saponite, montmorillonite (MX-80), [8] and mixed-layer clay [3] all with a dry bulk density of 1800 kg/m^3 at saturation. The tests refer to a shear stress corresponding to about 50 % of the shear strength.*

Clay	**Shear stress, kPa**	***A* *E-4**	***B* *E-4**	**t_o, s**
Saponite	220	-122	1	52766
Mixed-layer	297	-12	2	2800
Montmorillonite (MX-80), Na	188	-47	8	958
Montmorillonite (MX-80), Ca	118	-30	10	859

The parameter *B*, which is a measure of the shear modulus with higher values indicating ductile behavior ductility and low values stiffness, is lowest for the saponite and highest for the montmorillonite. The latter are hence more ductile and, according to Eq.1 in Section 4.5.3 more apt to creep than the saponite and mixed-layer clays. Eq.1 also implies that high t_o-values yield low initial creep rates while low ones imply high initial creep rates. One concludes from this that montmorillonite is more disposed to creep than the other clays investigated.

Since kaolinite and palygorskite have not been investigated no definite assessment can be made with respect to creep. However, as outlined in Section 4.5.3, it is highly probable that the latter two clays show less creep strain than the smectites.

6 DISCUSSION AND CONCLUSIONS

6.1 General

The tentative assessment given in Table 3 in Section 4.7, i.e. that the five clay types are relatively similar with respect to the major physical properties, except for the "inert" kaolinite, is validated by the experimental studies referred to in Chapter 5. They may all be considered in the final selection of buffer material although additional testing of palygorskite and very fine-grained kaolinite is required before it can be decided whether these two clay type qualifiy.

6.2 Aspects on function

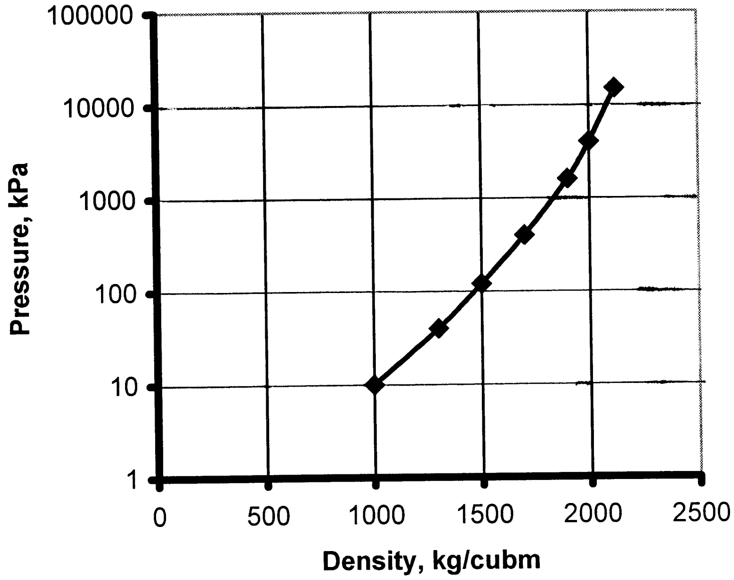
The reason why kaolinite has the lowest rank is because it has the highest hydraulic conductivity and the lowest expandability and hence poor self-healing properties, and also a very poor cation exchange capacity. It is interesting to see, however, that highly compacted kaolinite has recently been proposed as possible buffer clay candidate [30], on the ground that the hydraulic conductivity can be as low as E-13 m/s and that the shear strength is high and the compressibility low, meaning that the canister settlement will be very small. The preparation of the clay was made by consolidating a slurry of well dispersed kaolinite clay under 10 MPa pressure, yielding a void ratio of 0.5 and a density at saturation of 1900 kg/m^3. The presently reported conductivity of the slightly denser kaolinite clay, 2E-10 m/s, is due to the more heterogeneous microstructure that is caused by compacting clay powder [31]. Hence, kaolinite with its low anion diffusion capacity may not be ruled out.

The hydraulic conductivity of the smectitic clays, including the mixed-layer smectite-mica clay and palygorskite is sufficiently low to make make them acceptable and valuable as buffer material. Since this property has commonly been considered most important throughout the evolution of repository concepts it would be natural to select smectites as the most suitable material. However, it is associated with a swelling pressure that may be unacceptably high if the bulk density becomes too high either for manufacturing reasons or because of convergence of the deposition holes. This matter deserves attention and a basis for the assessment of buffers in the present context is the relationship between density at saturation and swelling pressure in Figures 23 and 24.

One finds from these diagrams that the swelling pressure of the montmorillonite-rich MX-80 clay rises continuously with increasing density for saturation with distilled water (Figure 23). However, if saturation takes place by uptake of Ca-rich groundwater there is an abrupt and steep rise from almost zero for about 1500 kg/m^3 to 10 MPa for about 2150 kg/m^3. At further rise in density the swelling pressure in the Ca-case increases very strongly and hence causes a risk of canister failure.

The corresponding relationship for palygorskite is even more dramatic as demonstrated by the diagram in Figure 24. The rise in swelling pressure at higher bulk densities than about 1600 kg/m^3 is very strong and it would be necessary to design a palygorskite buffer very carefully for fulfilling the criteria of minimum and maximum swelling pressure.

The mixed-layer smectite-mica clay appears to behave somewhat less dramatically as shown by the lowest diagram in Figure 24. One hence finds that an increase in bulk density at saturation from about 2000 to about 2100 kg/m^3 causes a rise in swelling pressure from about 1 to 2.5 MPa, and it is expected that a density of about 2200 kg/m^3 would not yield a swelling pressure of more than 10 MPa.



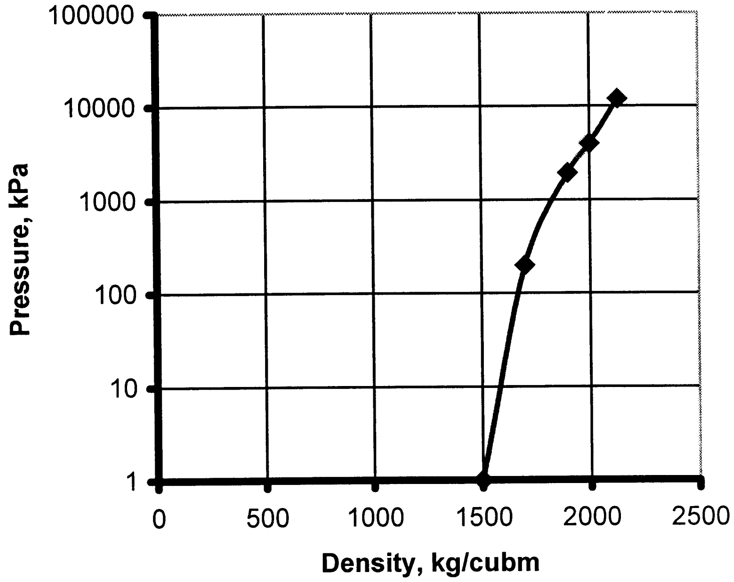


Figure 23. *Swelling pressure versus bulk density at saturation. Upper: MX-80 saturated with distilled water. Lower: MX-80 saturated with 3.5 % $CaCl_2$ solution..*

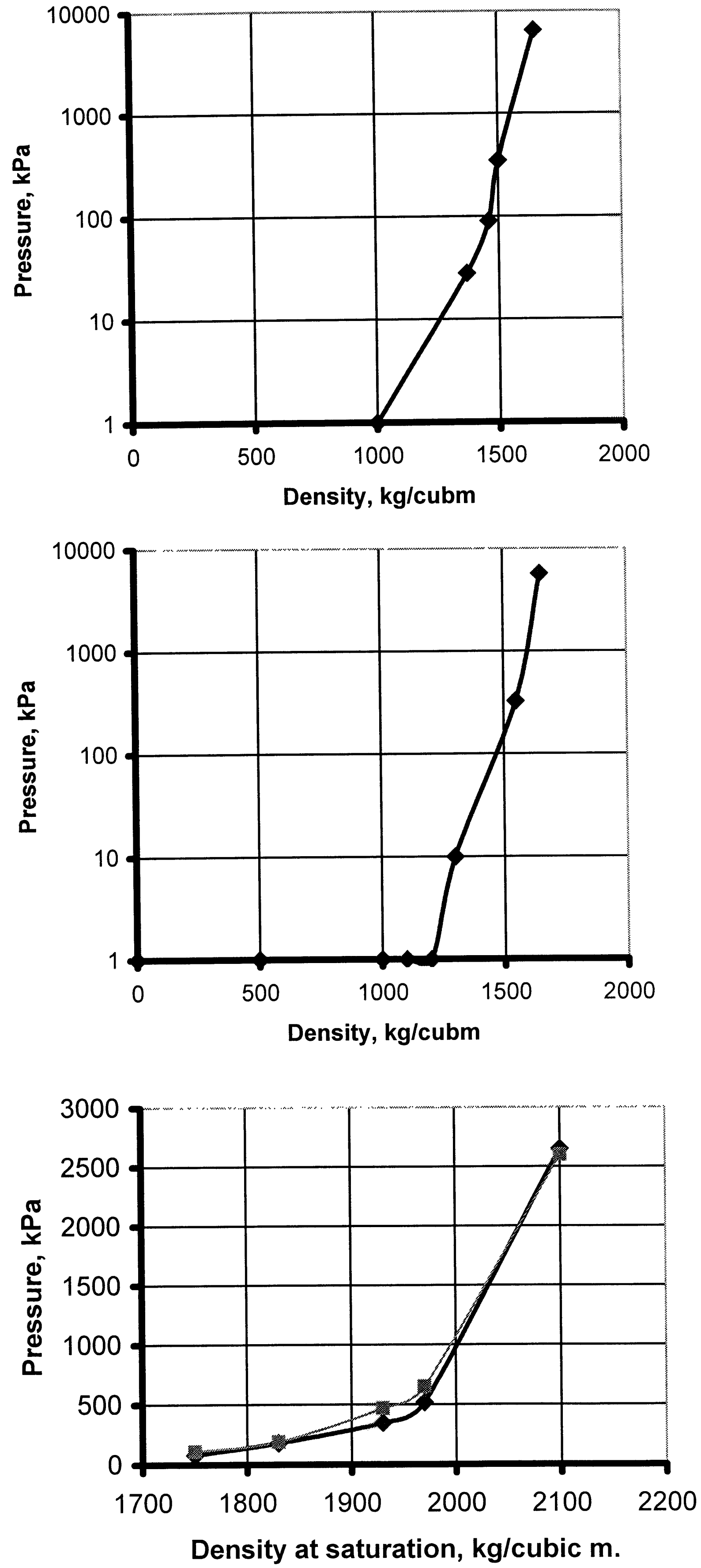


Figure 24. *Swelling pressure versus bulk density at saturation. Upper: Palygorskite saturated with distilled water. Middle: Palygorskite saturated with with 3.5 % $CaCl_2$ solution. Lower: Mixed-layer (Friedland clay). Thick line represents distilled water and thin line 3.5 % $CaCl_2$ solution.*

The matter of gas conductivity needs consideration in conjunction with the discussion of pressures. Thus, it is not yet certified that smectite-rich buffer clays really let gas through at a pressure corresponding to the swelling pressure or less than that. More testing is hence required of all possible candidate buffers but it is believed that, for microstructural reasons, the critical gas pressure of the mixed-layer smectite-mica as well as the kaolinite and palygorskite clays will be lower than that of the smectite-rich ones.

6.3 Final comments

The present investigation brings one to conclude that SKB's candidate buffer clay MX-80 and also saponite are very suitable and would work well in a repository. Still, it is clear that other clays, particularly the less smectitic but significantly expandable and low-permeable mixed-layer smectite-mica Friedland clay is a strong candidate because of its thermal and rheological properties. Palygorskite has a number of good properties and would be useful as buffer material but its swelling pressure may be an obstacle.

The Friedland clay is considered here as the main competitor of the smectites for use as buffer. It is available in very large quantities and has been found to be a good alternative of tunnel and shaft backfills [11]. The present cost level is very attractive and further investigation of this clay material seems to be worth while. Such extended work should comprise both more detailed examination of its physical and chemical properties and also whether large stable blocks can be prepared. A preliminary study of the clay has been reported [32] and it has shown that the density of blocks obtained by compacting fine powder yields a density that will be about 2340 kg/m^3 after saturation (Figure 25).

Figure 25. *Block of Friedland clay prepared by compacting powder with about 3 % water content under 100 MPa pressure. The diameter and height are 28 and 9.8 cm, respectively [33].*

This is because of the excellent compaction properties reduce the pore space to a lower value than for the more smectite-rich clays like MX-80 smectite and that is expected to give as low hydraulic conductivity as of this clay type (Figure 26). A bulk density at saturation of 2150-2200 kg/m^3 is assumed to make buffer of this type as tight as that of MX-80, but the swelling pressure needs to be checked.

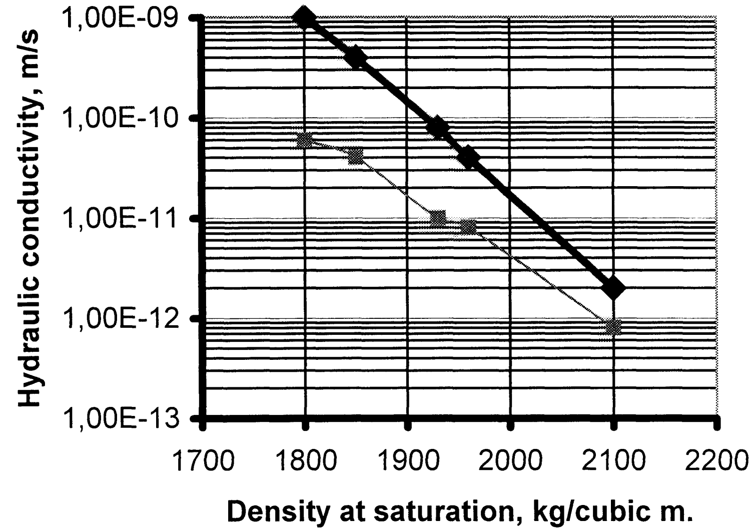


Figure 26. Hydraulic conductivity of Friedland clay for different densities at water saturation. The thin line represents percolation with distilled water while the thick line represents 3.5 % $CaCl_2$ solution.

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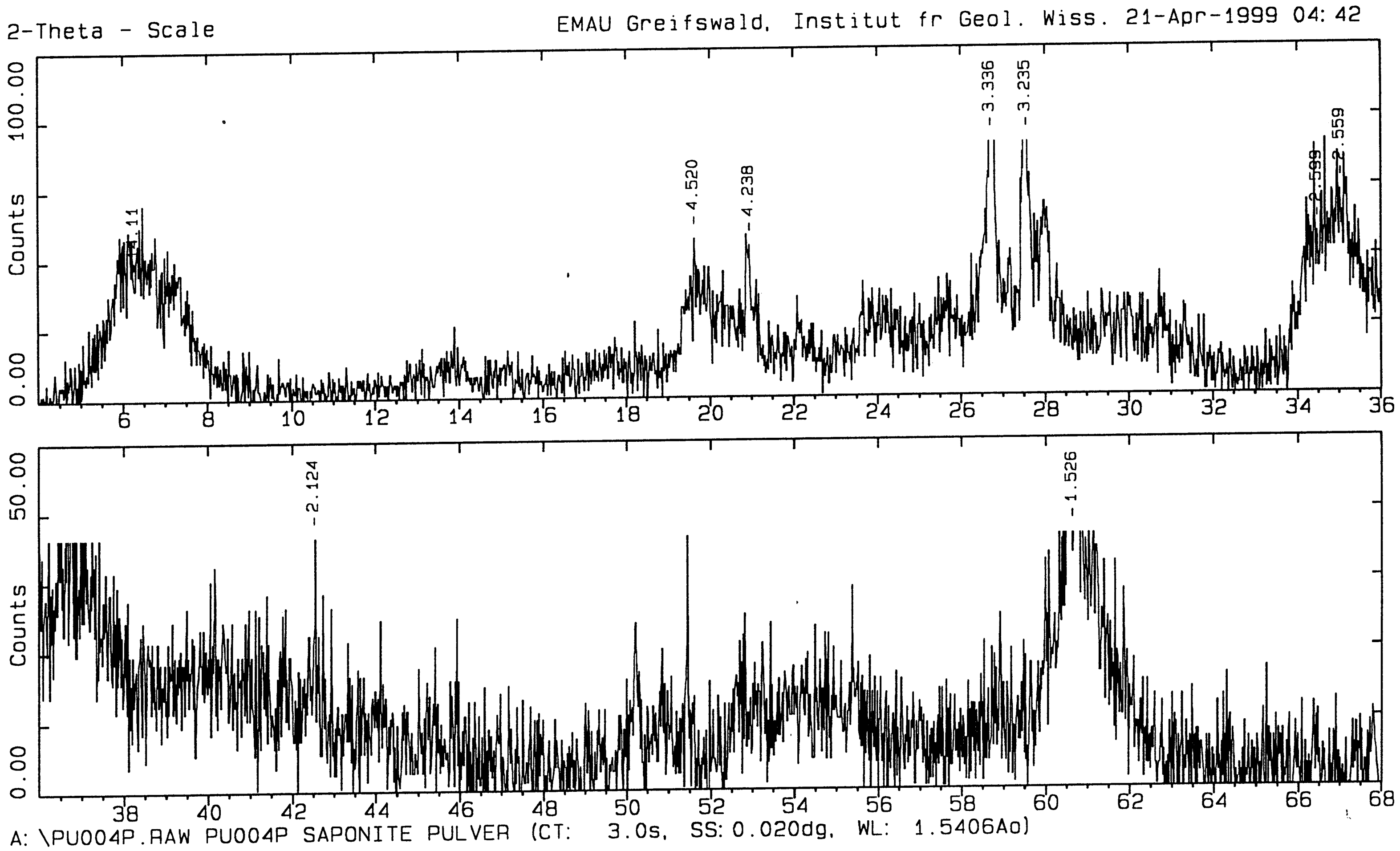
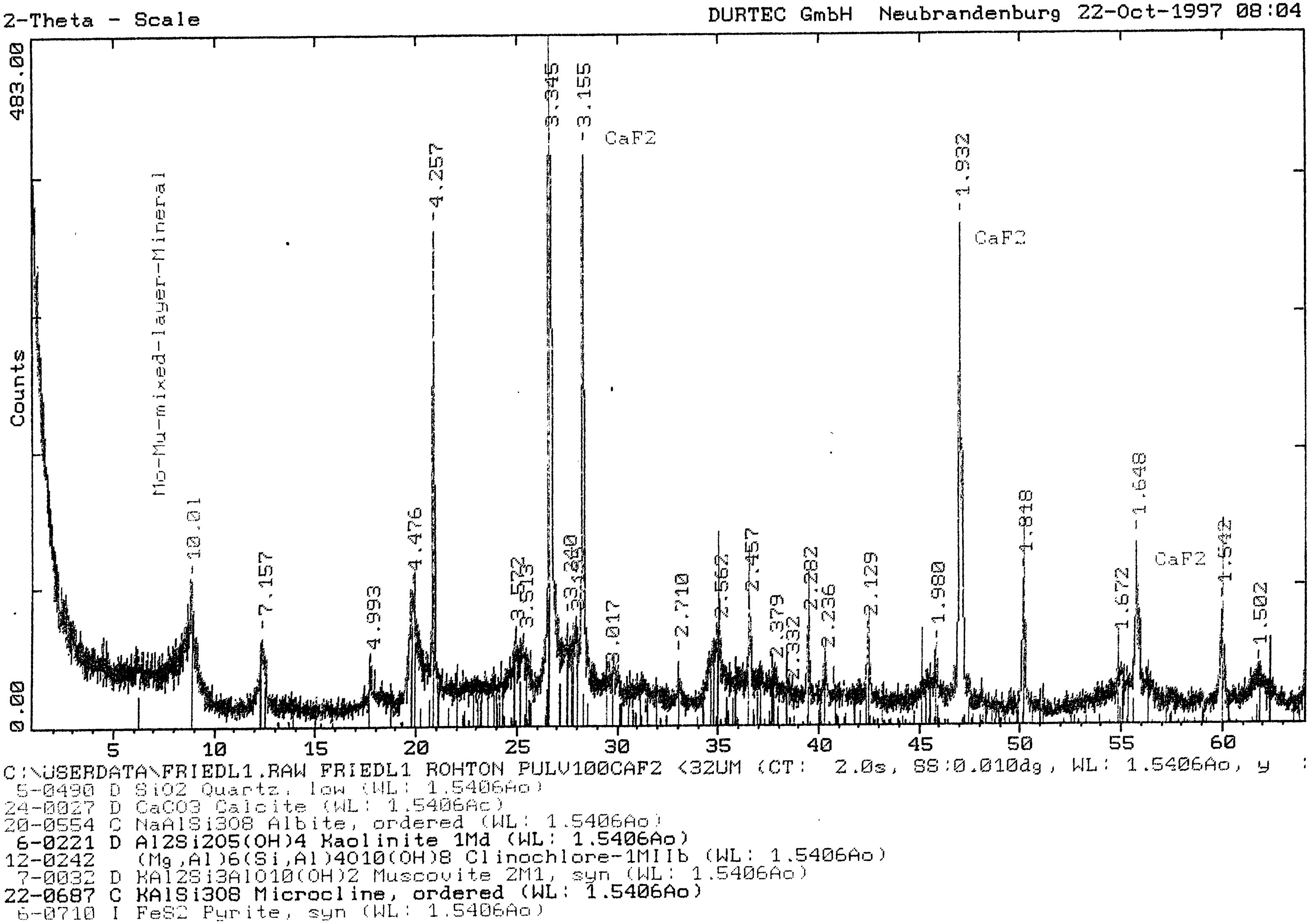
APPENDIX – XRD SPECTRA

SAPONITE (Untreated)



MIXED-LAYER SMECTITE-MICA
(Untreated Friedland clay)



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 5-0490 D SiO2 Quartz, low (WL: 1.5406Ao)
24-0027 D CaCO3 Calcite (WL: 1.5406Ac)
20-0554 C NaAlSi3O8 Albite, ordered (WL: 1.5406Ao)
 6-0221 D Al2Si2O5(OH)4 Kaolinite 1Md (WL: 1.5406Ao)
12-0242   (Mg,Al)6(Si,Al)4O10(OH)8 Clinochlore-1MIIb (WL: 1.5406Ao)
 7-0032 D KAl2Si3AlO10(OH)2 Muscovite 2M1, syn (WL: 1.5406Ao)
22-0687 C KAlSi3O8 Microcline, ordered (WL: 1.5406Ao)
 6-0710 I FeS2 Pyrite, syn (WL: 1.5406Ao)
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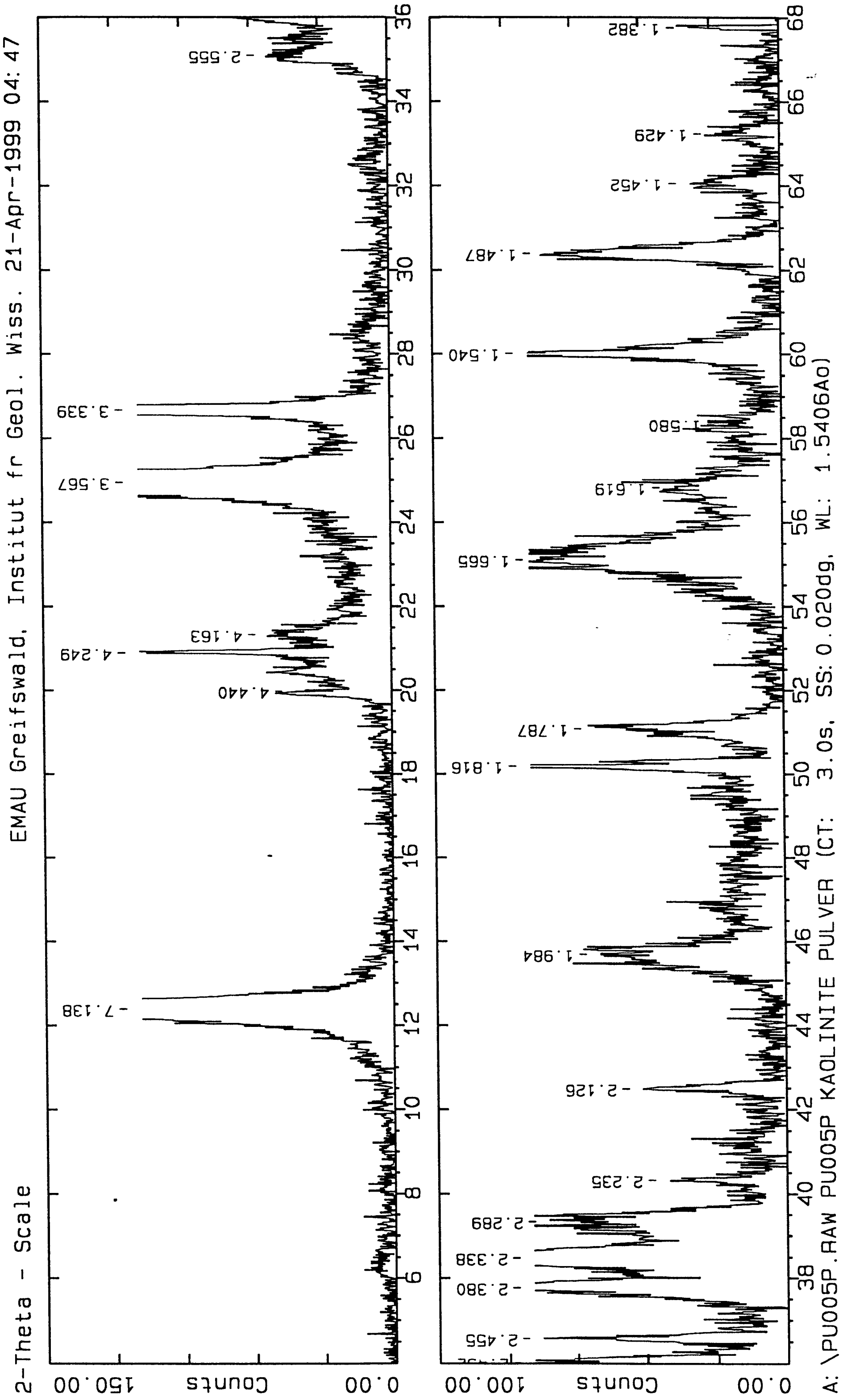
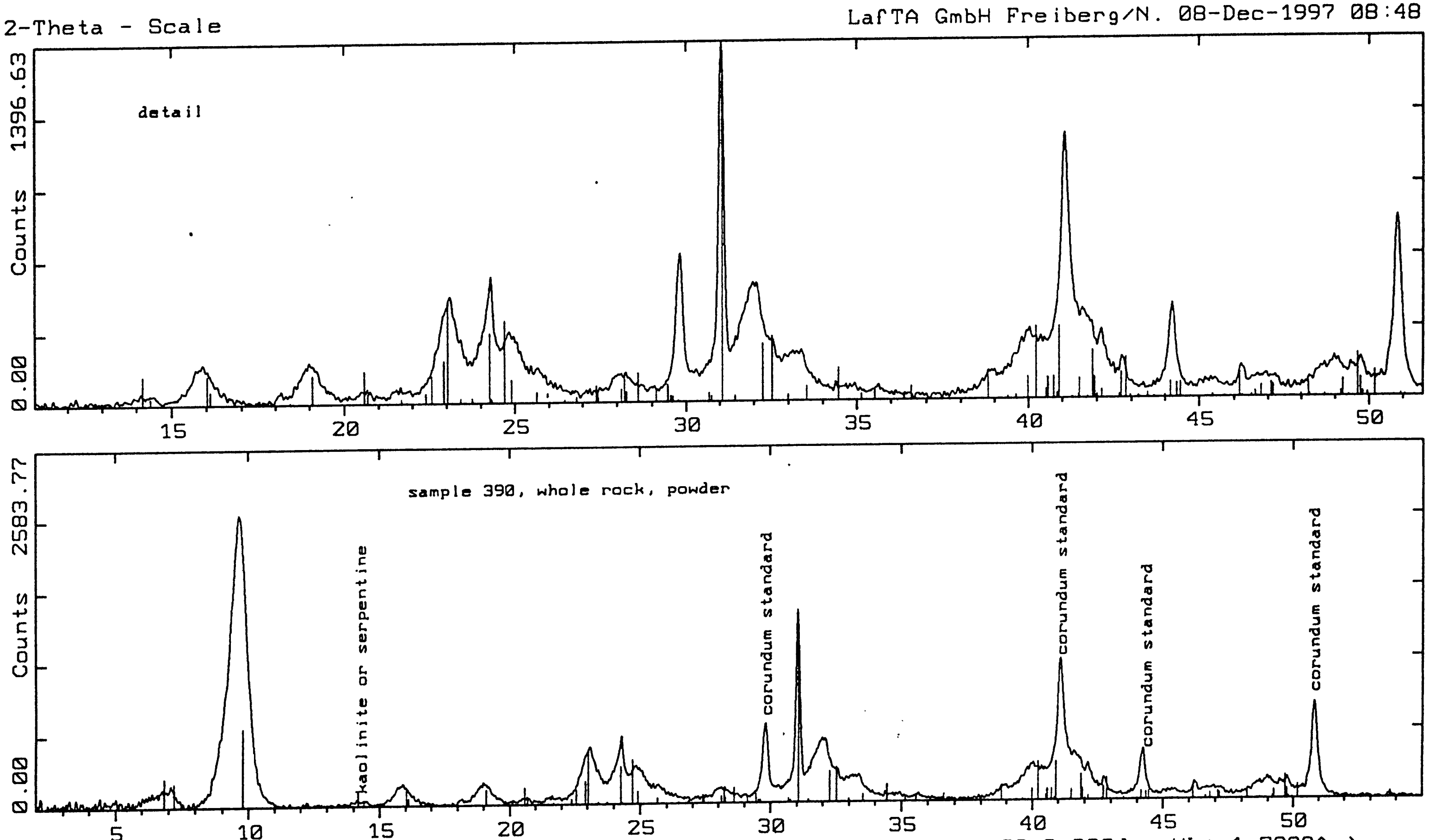
KAOLINITE (Untreated)



PALYGORSKITE (Untreated)



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C:\DATEN\POWDER\9711243K.RAW 9711243K PUSCH390+20%KORUND (CT:  3.0s, SS:0.020dg, WL: 1.7890Ao)
20-0688 D Mg5Si8O20(OH)2.8H2O Palygorskite (WL: 1.7890Ao)
13-0135   Ca0.2(Al,Mg)2Si4O10(OH)2.xH2O Montmorillonite-15A (WL: 1.7890Ao)
33-1161 * SiO2 Quartz, syn (WL: 1.7890Ao)
29-0713 I FeO(OH) Goethite (WL: 1.7890Ao)
16-0613 I Mgx(Mg,Fe)3(Si,Al)4O10(OH)2.4H2O Vermiculite-2M (WL: 1.7890Ao)
 9-0466 * NaAlSi3O8 Albite, ordered (WL: 1.7890Ao)
11-0386   (Mg,Al)3(Si,Al)2O5(OH)4 Lizardite-1T, aluminian (WL: 1.7890Ao)
```

MONTMORILLONITE (MX-80)

(Untreated and glycolated)